Looking for Leverage

in

New ARPES Beamlines

National Synchrotron Light Source II Workshop

Session on “Photoemission”

Wednesday, July 18, 2007

Funding support: U.S. NSF and U.S. Dept. of Energy

and Advanced Light Source Doctoral Fellowship Program

OR

National Synchrotron Light Source II Workshop

Session on “Photoemission”

Wednesday, July 18, 2007

Funding support: U.S. NSF and U.S. Dept. of Energy

and Advanced Light Source Doctoral Fellowship Program

Some experiences with assessing and avoiding surface effects in photoemission spectroscopy of correlated electron materials

National Synchrotron Light Source II Workshop

Session on "Photoemission"

Wednesday, July 18, 2007

Funding support: U.S. NSF and U.S. Dept. of Energy

and Advanced Light Source Doctoral Fellowship Program

Collaborators

S.-K Mo*	*University of Michigan* (*now *Stanford* and *ALS*)
Feng Wang	*University of Michigan*
J.D. Denlinger	*Advanced Light Source, LBNL*
G.-H. Gweon	*University of California, Santa Cruz*
Kai Rossnagel	*University of Kiel*
S. Suga and A. Sekiyama	*Osaka University*
H.-D Kim, J.-H. Park	*Pohang University, Pohang Synchrotron*
M. B. Maple	*University of California, San Diego*
Z. Fisk	*University of California, Irvine*
J. Sarrao	*Los Alamos National Laboratory*
P. Metcalf	*Purdue University*
A. B. Shick	*ASCR – Prague*
H. Yamagami	*Kyoto-Sangyo University*
D. Vollhardt, G. Keller, V. Eyert	*University of Augsburg*
K. Held	*Max-Planck Institute, Stuttgart*
V. I Anisimov	*Institute of Metal Physics, Ekaterinburg*
B. Delley	*Paul-Scherrer Institute*
R. Monnier	*ETH-Zurich*

electron removal (and addition) to study single-particle behavior of many-body system

Spectroscopy of energy and momentum dependence of spectral weight

$$\rho\,(k,\omega) = \quad (1/\pi)\ \mathrm{Im}\,[1/\,(\omega - \varepsilon_k - \Sigma(k,\omega))]$$

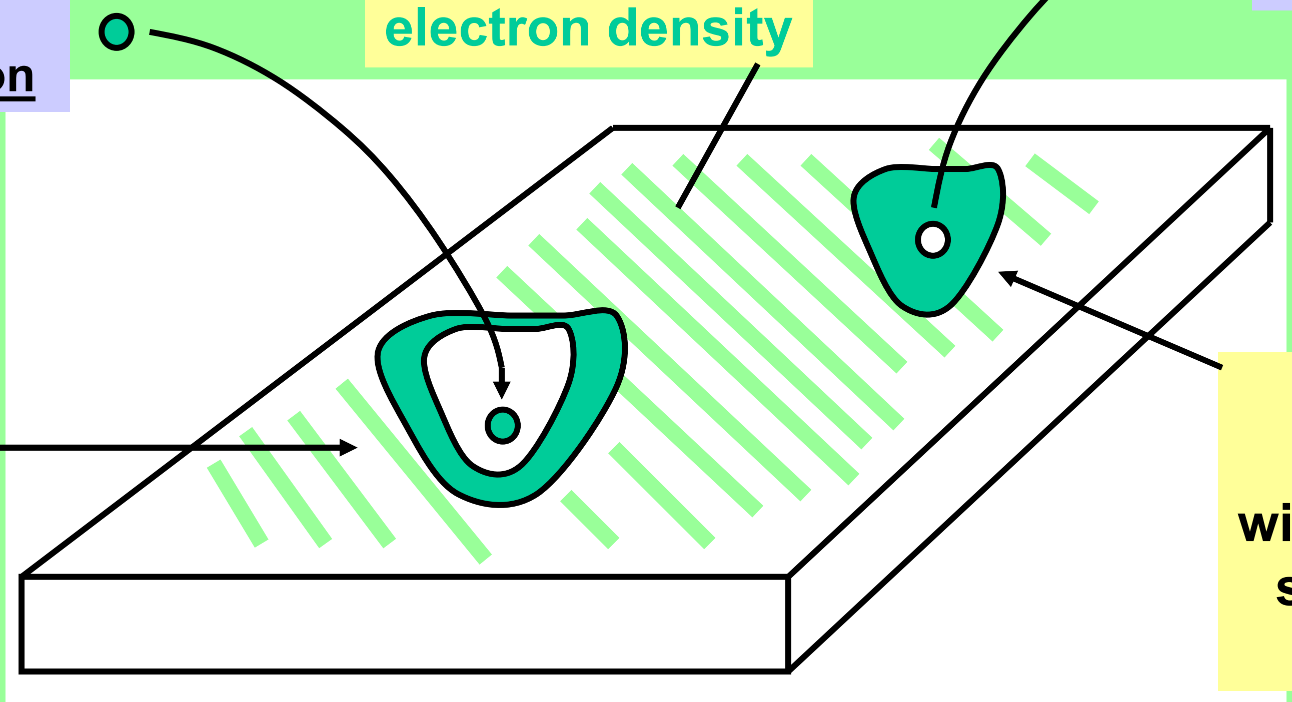
of single particle Green's function

Insert e –
from ∞
<u>inverse</u>
<u>photoemission</u>

sample with
ground state
electron density

remove e – to ∞

<u>photoemission</u>



added
electron
with
hole
screening
cloud

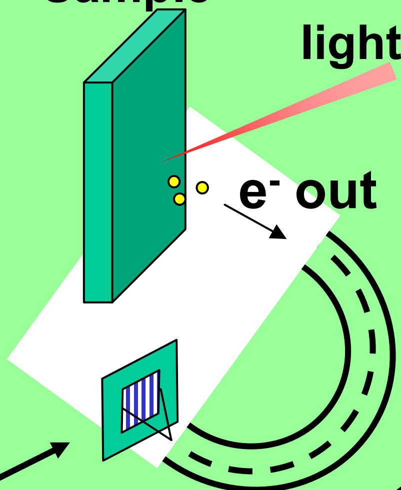
added
hole
with electron
screening
cloud

Both processes together give unbound hole/electron pair
the RIGHT WAY TO DEFINE INSULATOR GAP!

Einstein's photoelectric effect to measure removal part of $\rho(k,\omega)$

Sample

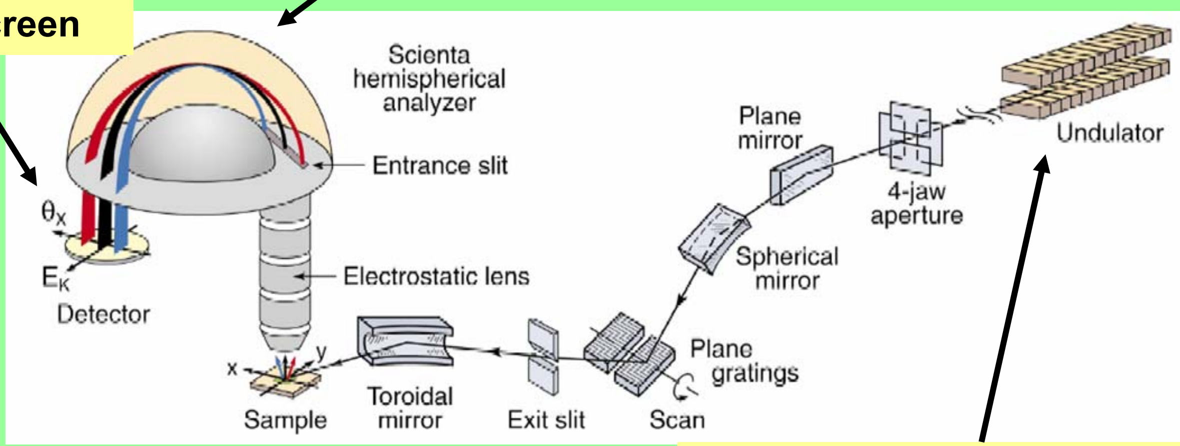
light in



e^- out

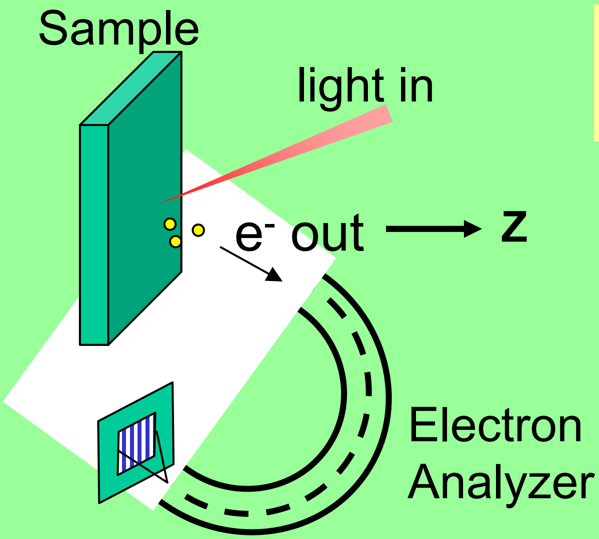
Electron Analyzer

Detector screen



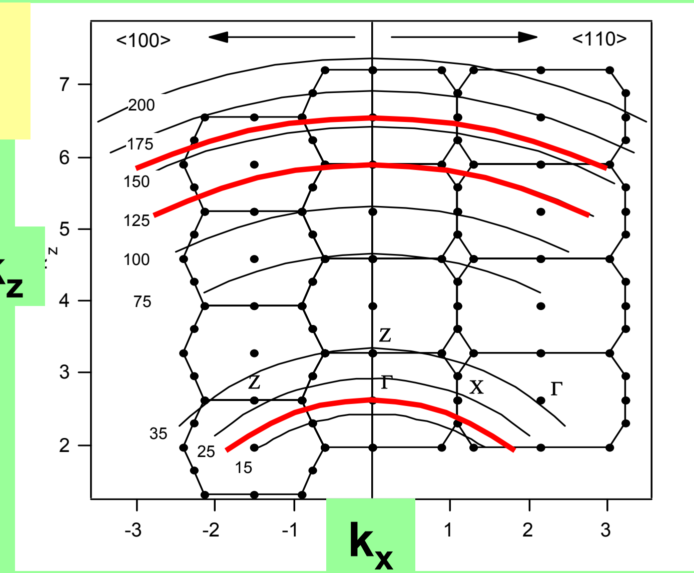
Undulator device inserted in synchrotron electron beam gives intense light.

Photoemission spectroscopy (and its inverse) to measure $\rho(k,\omega)$ or k-summed $\rho(\omega)$

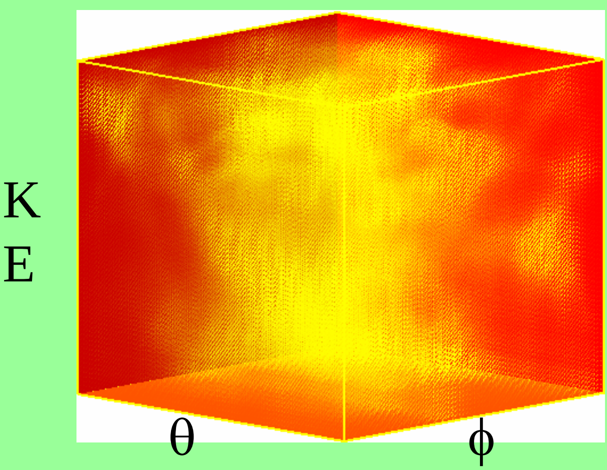


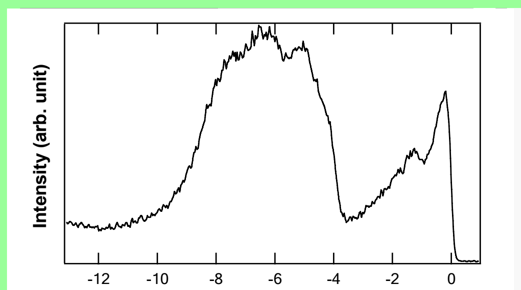
Angle variation moves on spherical k-space surfaces.

Vary photon energy to change k_z



Full electronic structure @ fixed photon energy —3D data set—

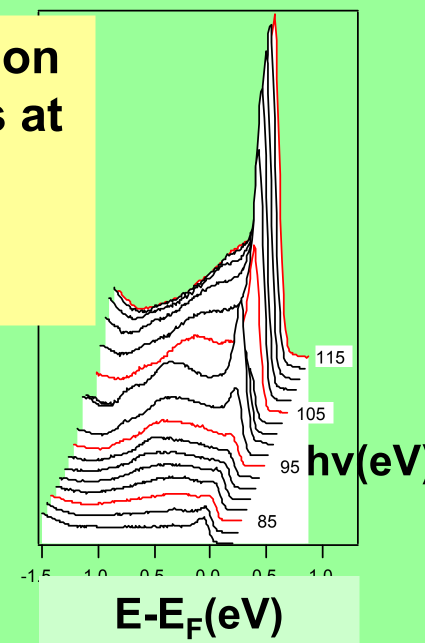




Angle integrated Or k-summed

Cross-section resonances at core level absorption edges

= RESPES



angles, energies $\Rightarrow$ k

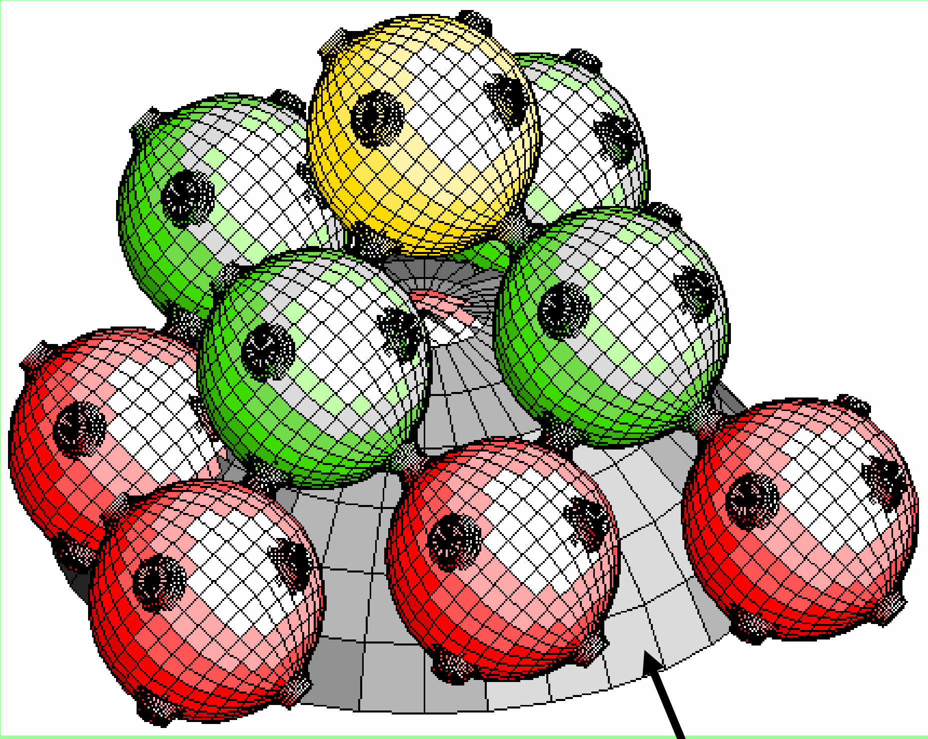
High photon energy gives Larger elastic escape depth $\Rightarrow$ Greater bulk sensitivity

Fermi Surface Mapping of a 3D metal

ALS – early 1990's
E. Rotenberg, J. D. Denlinger

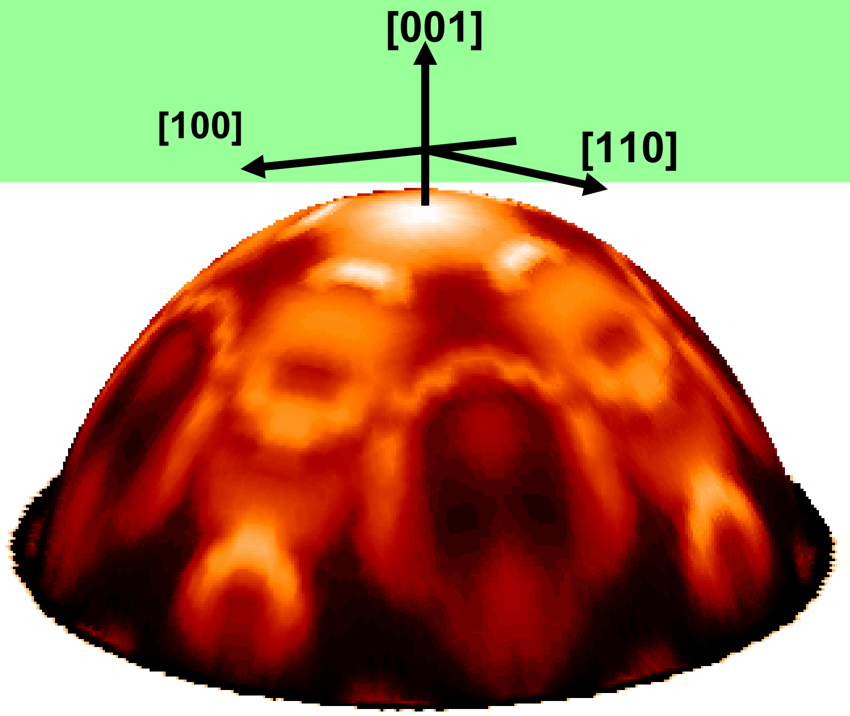
BERKELEY LAB

k-space (repeated zones)



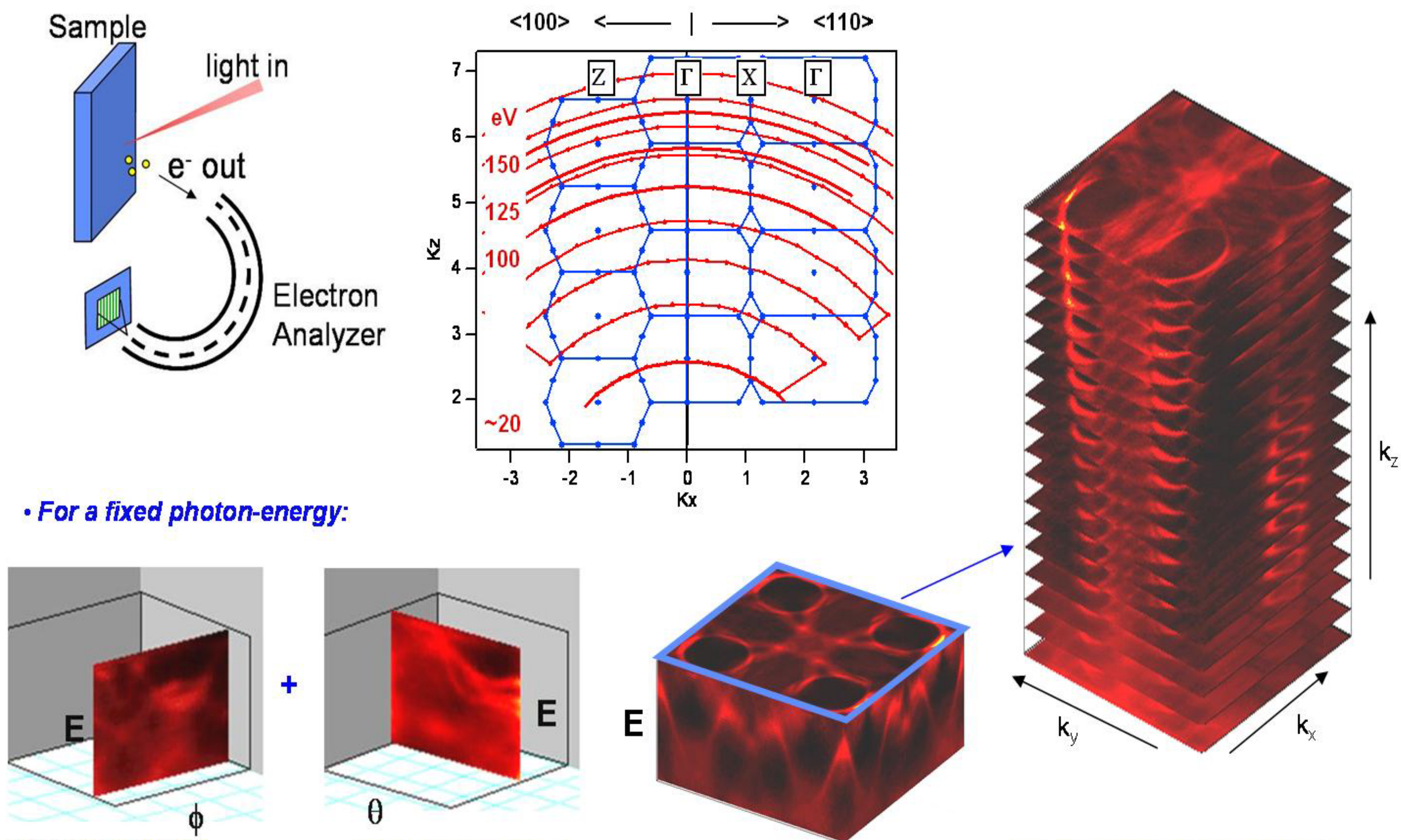
Constant energy measurement surface

Cu (100) hν=83 eV



- Plane wave final state
- Surface refraction included *(inner potential = 8.8 eV)*

ARPES data acquisition for three dimensional materials



(1) Parallel angle detection
(unit of acquisition)

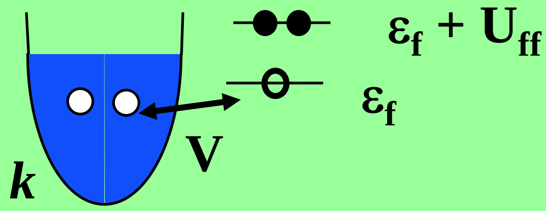
(2) Vary sample or detector angle

(3) Assemble volume electronic structure

(4) Extract E_F slice, i.e. "Fermi Surface" map

(5) Assemble hv-dependent 3D data set of FS maps

Anderson impurity model and emergent Kondo behavior



D(ε)

occupation n_f
near 1 for Ce^{3+}

<u>N_f fold degenerate local orbital hybridized to conduction band</u>

- Binding energy ε_f
- Hybridization $\Delta(\varepsilon) = \pi D(\varepsilon)\, V(\varepsilon)^2$
- Local Coulomb Interaction U_{ff}
- Spin orbit splitting Δ_{LS}

<u>Low Energy Scale T_K:</u>

($U_{ff} \to \infty$, $f^0 \leftrightarrow f^1$, $\Delta_{LS}=0$,)

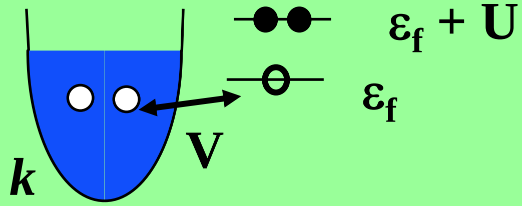
$k_B T_K = E_F \exp(-1/J)$

$J = N_f\, \Delta / \pi \varepsilon_f$

Very fast dependence on J !

- Ground State Singlet
- Spin entropy quenched
  for $T \ll T_{Kondo}$

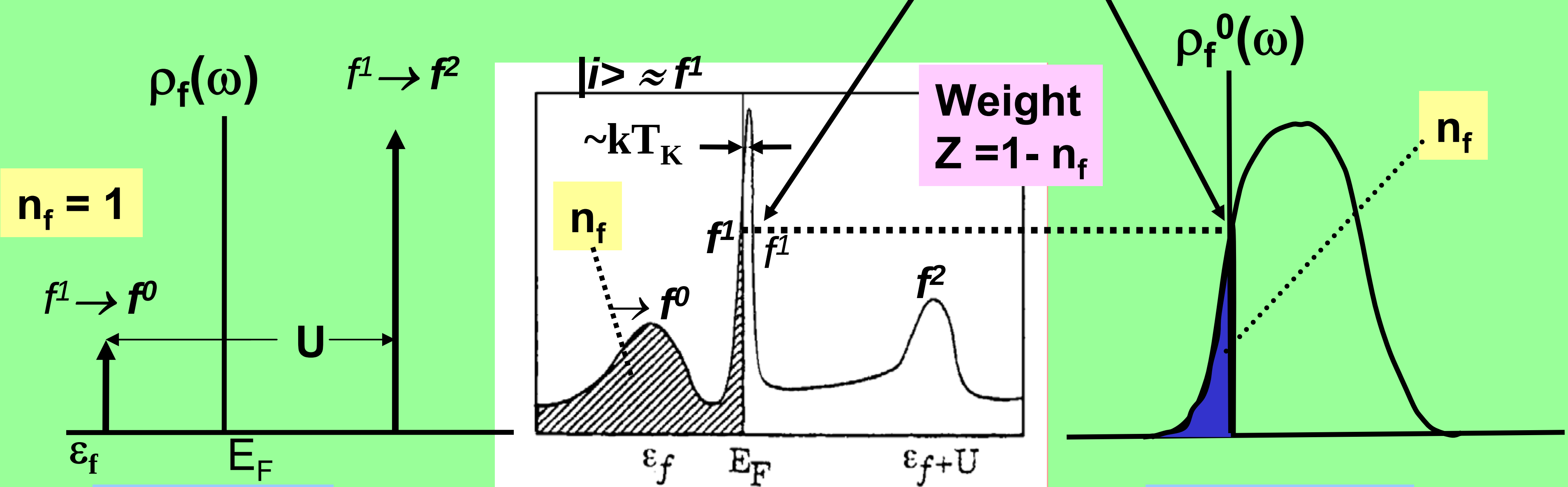
Quasi-particle of Anderson impurity model



Kondo / Suhl-Abrikosov resonance

a Fermi energy peak implied by Friedel Sum Rule (Langreth) for fixed n_f

$$\rho_f(\omega = E_F) = \rho_f^0(\omega = E_F)$$



V=0, U≠ 0
f^1 moment

U, V ≠ 0
no moment

U = 0, V ≠ 0
no moment

Effective mass = band mass / Z   Can be very large for small T_K

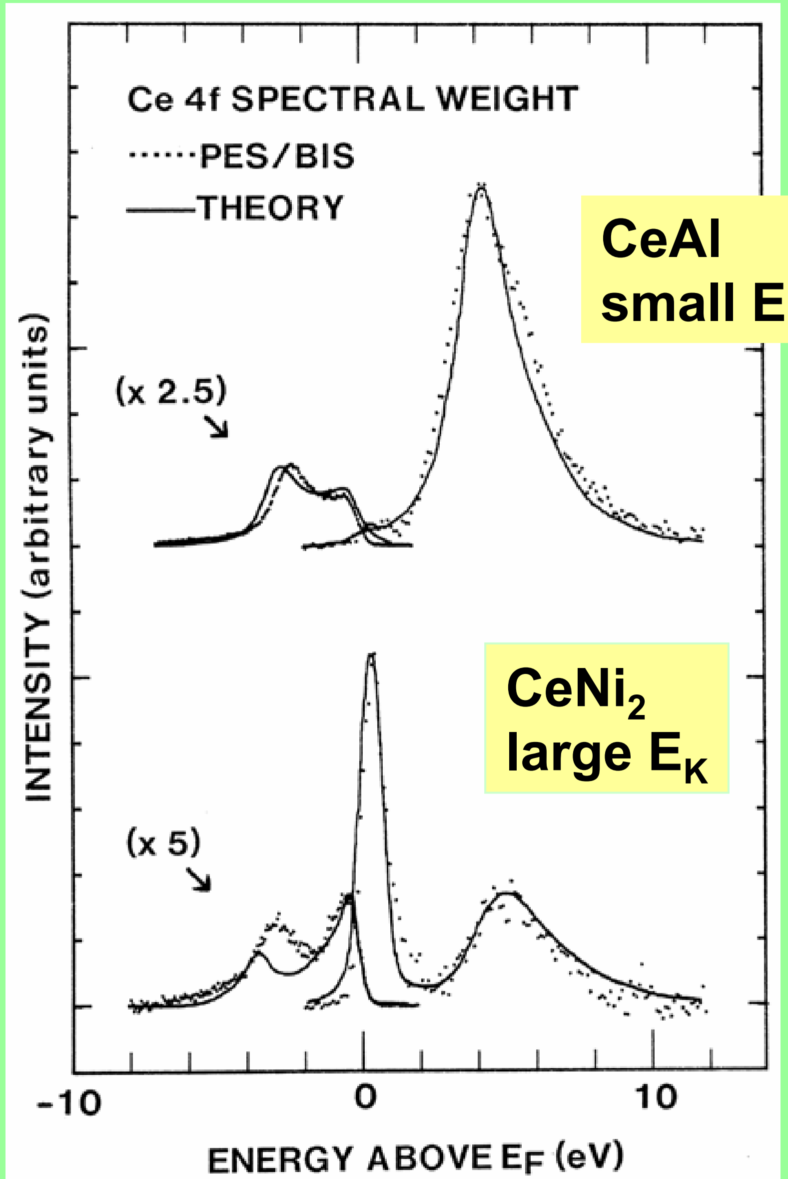
Kondo resonance in angle integrated Ce 4f spectra: early experiment and theory -- large m ⇔ small T_K

Spectra from photoemission

and x-ray inverse photoemission (Xerox PARC)

samples: (Maple, UCSD)

Allen et al PRB 1983



CeAl small E_K

$CeNi_2$ large E_K

Fig. from Allen et al Adv. in Physics 1985

Spectral theory: Gunnarsson & Schönhammer PRL 1983

“Kondo Volume Collapse”

Ce α phase E_K large

γ phase E_K small

Allen & Martin PRL ’82

Allen & Liu PRB ‘92

Some historical perspective

Fallout from Ce RESPES on 2 eV binding energy
and Kondo resonance findings of 1978-1981

- You don't measure the right thing.
  "Not the binding energy in the ground state."
  "High energy photon too brutal for delicate Kondo physics"
  fundamental misunderstandings--mostly gone now.

- You have crummy resolution. wow, Scienta

- Couldn't you do it k-resolved? making real progress.

- You only measure the surface. even larger issue now
  (Suga SPring-8 beamline really important step forward)

“Surface tension in bulk spectroscopy”

<u>Ever more important exactly because of</u>:

- **improved resolution**
- **emphasis on ARPES**
- **more sophisticated questions asked—**
  e.g. Fermi surfaces, lineshapes, FL vs. NFL

<u>Two general issues:</u>

- **surface/bulk electronic structures, how different?**
- **surface inhomogeneous?**

Surface effects

<u>My General Impressions:</u>

- **understanding for solid samples still mostly ad hoc, empirical, but starting to understand some principles**

- **microscopy really scary—but also correlation between spectrum quality and visual appearance low**
  e.g. Seamus Davis STM for cuprates

- **small measurement area really important**

- **still must consider on <u>case by case basis</u> ---**
  can't reliably predict or generalize

Surface effects – some general principles

Reduced coordination the basic origin of bulk/surface difference

Surface states from altered potential

long lived if occur in energy gap
of bulk band structure projected to surface

study theoretically with repeated slab calculations

Particularly likely on polar non-neutral surfaces

Surface effects for strongly correlated systems

Reduced coordination the basic origin of bulk/surface difference

- **Reduces bandwidth on surface**

  $\Rightarrow$ **reduced t/U**

- **Surface cohesive energy less than bulk**

  $\Rightarrow$ **surface binding energy |E| of local orbital increased**

  B. Johansson, PRB 19, 6615 (1979)

  and so ….

  |E(corner atom)| > |E (edge atom)| > |E(smooth surface)|

Experimental Verification by M. Domke et al, PRL 56, 1287 (1986)

Smooth Tm metal surfaces: shifted surface trivalent peaks

Rough Tm metal surfaces: also show trivalent peaks

Mott-Hubbard metal-insulator transition

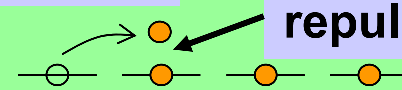
new view from "Dynamic Mean Field Theory"

(Vollhardt, Metzner, Kotliar, Georges ≈ 1990)

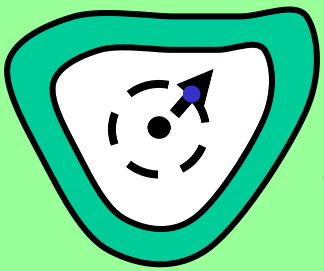
DMFT: lattice ⇒ a <u>self-consistent</u> Anderson impurity model (exact in ∞ dimensions -- finds $\Sigma(k,\omega) = \Sigma(\omega)$)

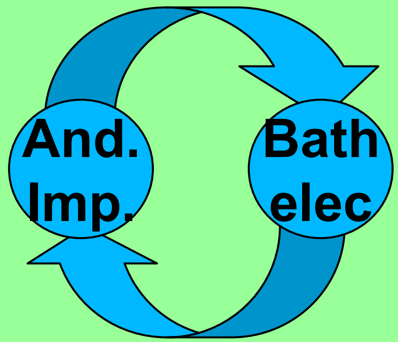
hopping t

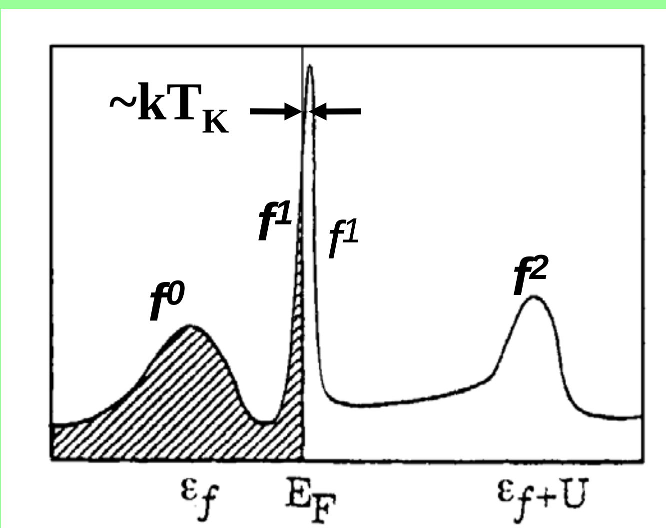
repulsion U



Hubbard model for Mott transition



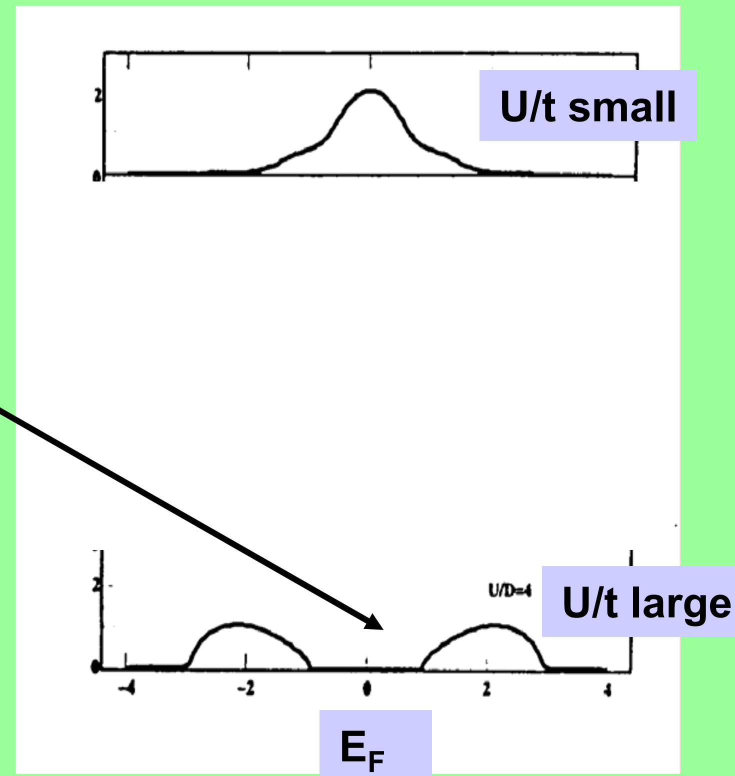




Kondo physics—moment loss & Suhl-Abrikosov/Kondo resonance

Gap in electron addition/removal spectrum due to U

gives insulator!

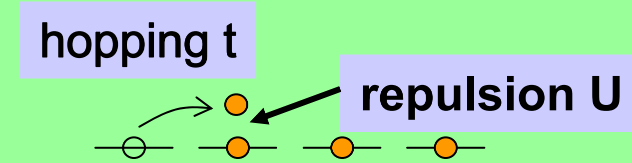


Mott-Hubbard metal-insulator transition

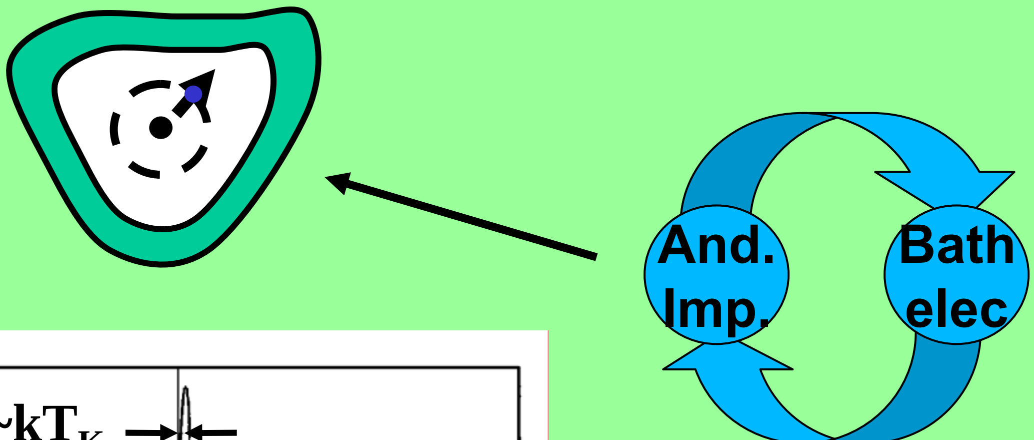
new view from Dynamic Mean Field Theory

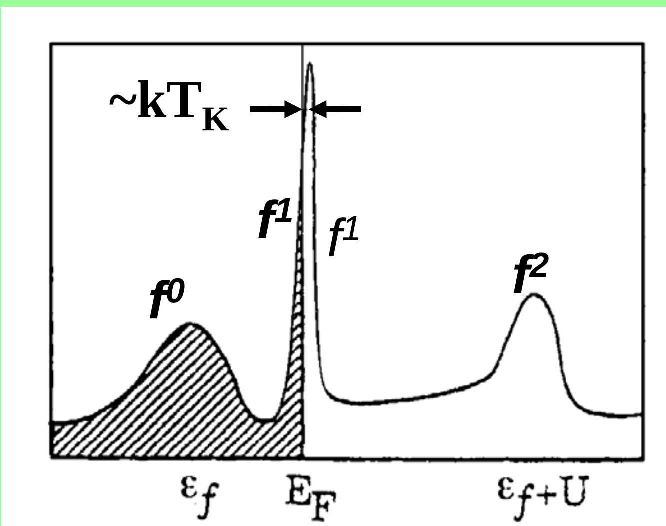
(Vollhardt, Metzner, Kotliar, Georges ≈ 1990)

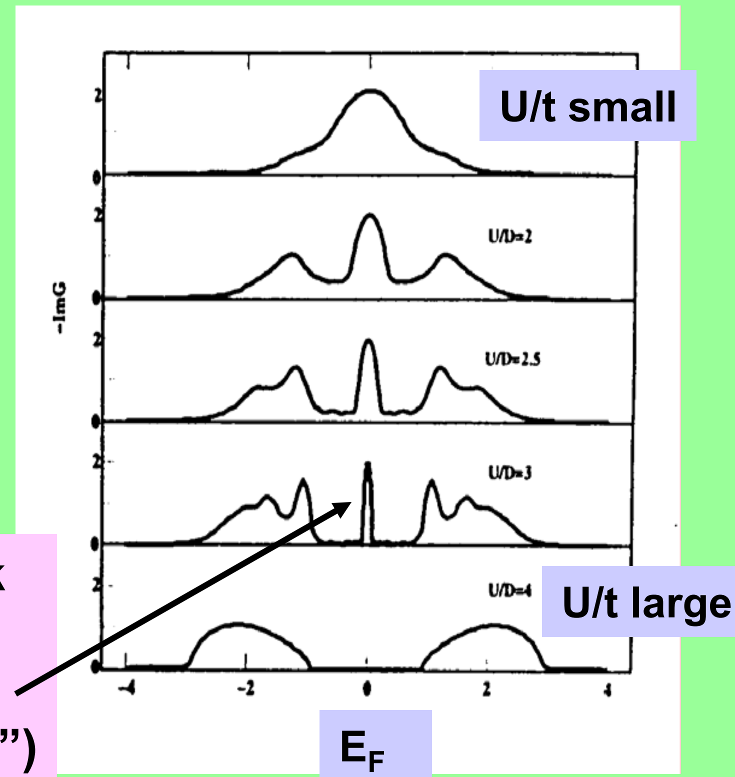
DMFT: lattice $\Rightarrow$ a <u>self-consistent</u> Anderson impurity model (exact in ∞ dimensions -- finds $\Sigma(k,\omega) = \Sigma(\omega)$)



Hubbard model for Mott transition



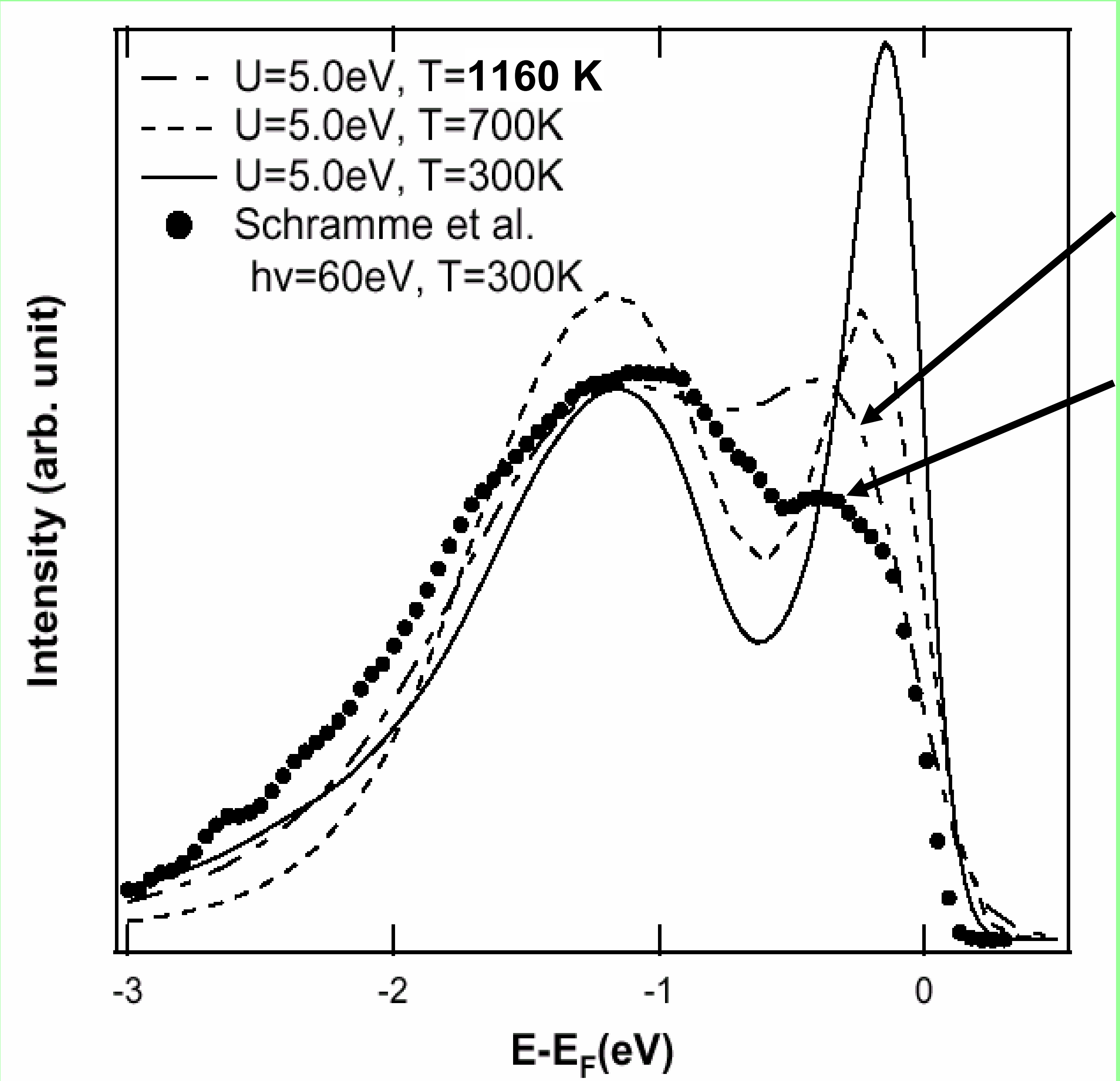




quasi-particle peak growing in gap as U/t decreases ("bootstrap Kondo")

Kondo physics—moment loss & Suhl-Abrikosov/Kondo resonance

T-dependent LDA +DMFT(QMC) theory compared to PM phase low hν photoemission for V_2O_3



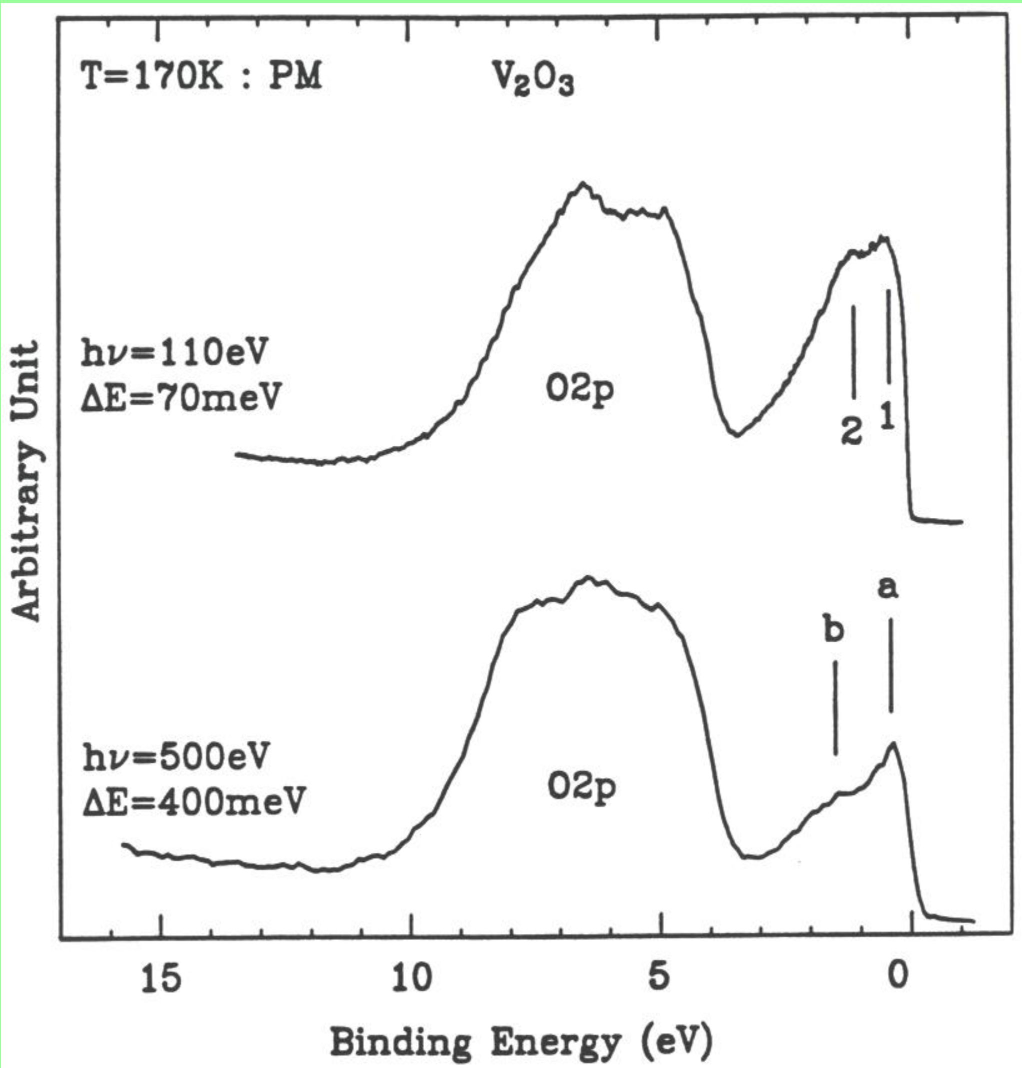
LDA + DMFT (QMC) at 1160K

compared favorably to 300K 60 eV data (Held et al, PRL '01)

But theory peak sharpens up with decreasing T

Shows large disagreement with data for same T.

Early evidence of bulk/surface difference for V_2O_3



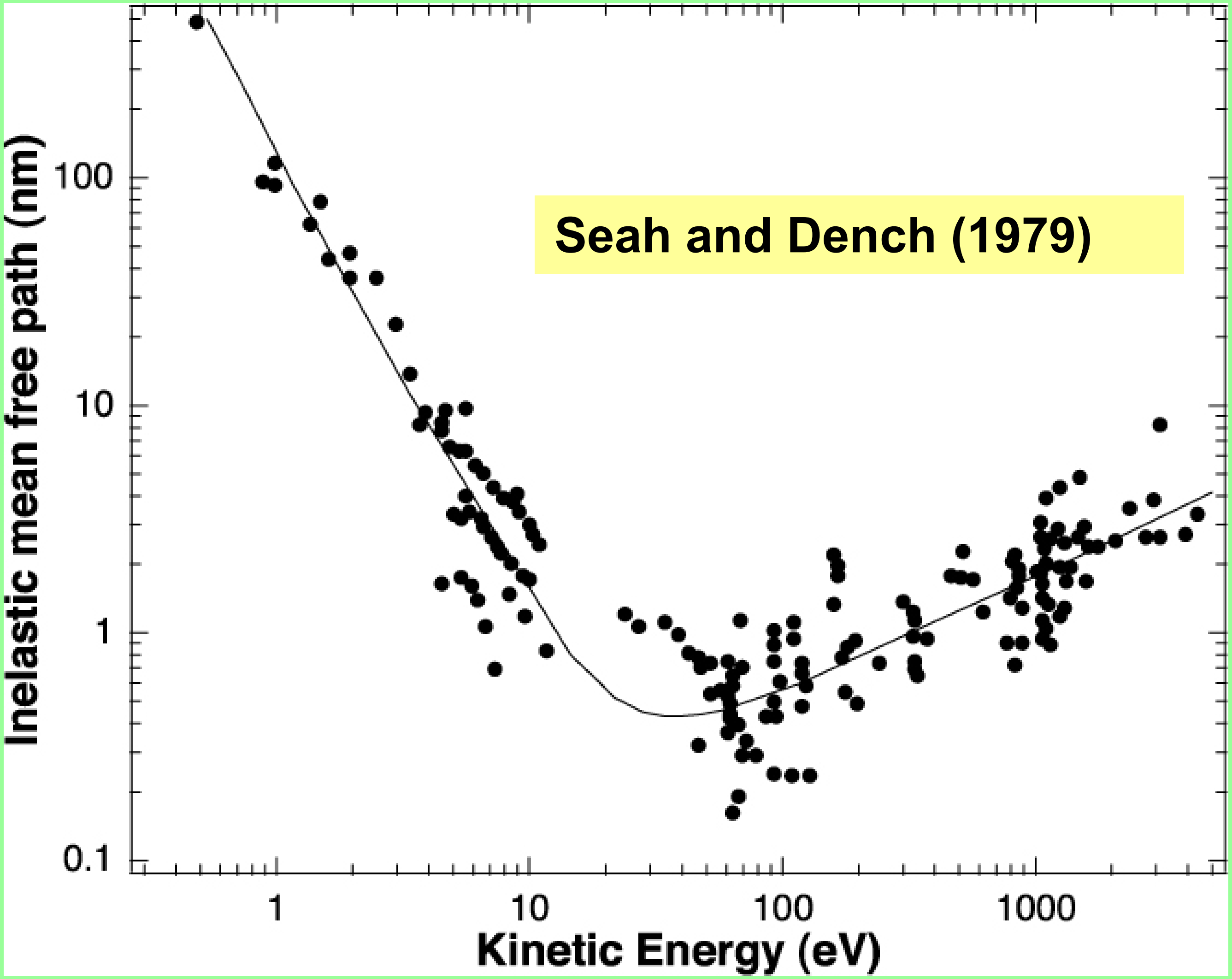
J.-H. Park thesis
NSLS "dragon" beamline
(Univ. of Michigan 1994)

Systematic reduction of near E_F peak in metallic phase for low photon energy relative to high photon energy

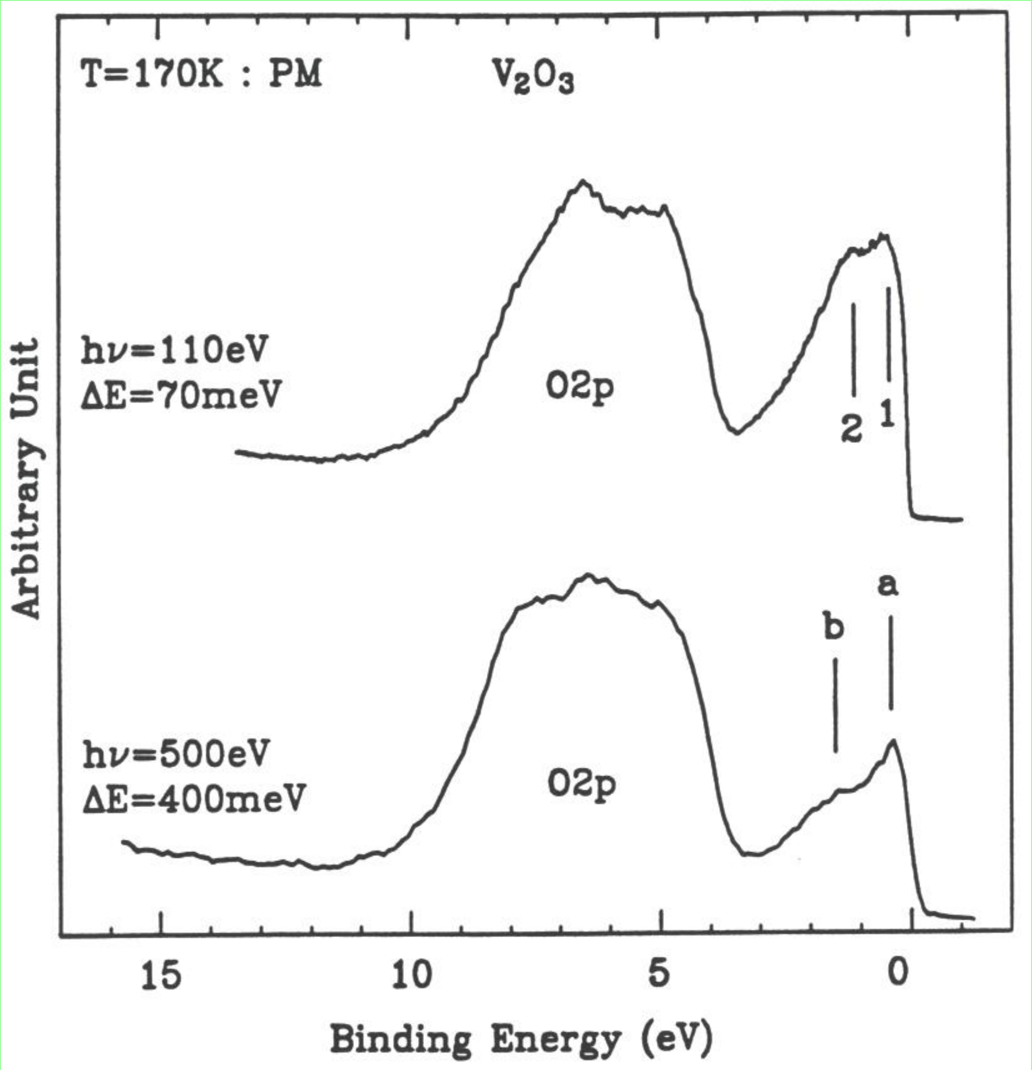
implies surface effect

Qualitative energy dependence of inelastic mean free path

Curve not really "universal"



Early evidence of bulk/surface difference for V_2O_3



J.-H. Park thesis
NSLS "dragon" beamline
(Univ. of Michigan 1994)

Systematic reduction of near E_F peak in metallic phase for low photon energy relative to high photon energy

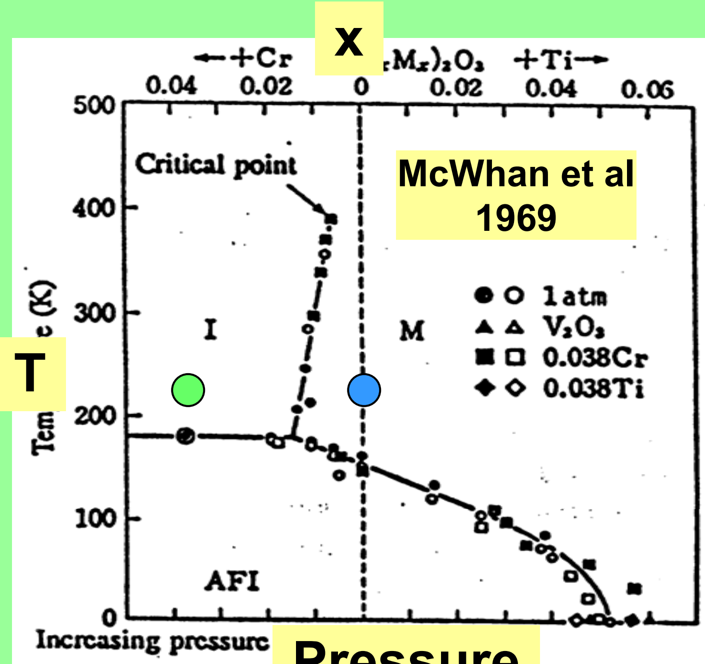
implies surface effect

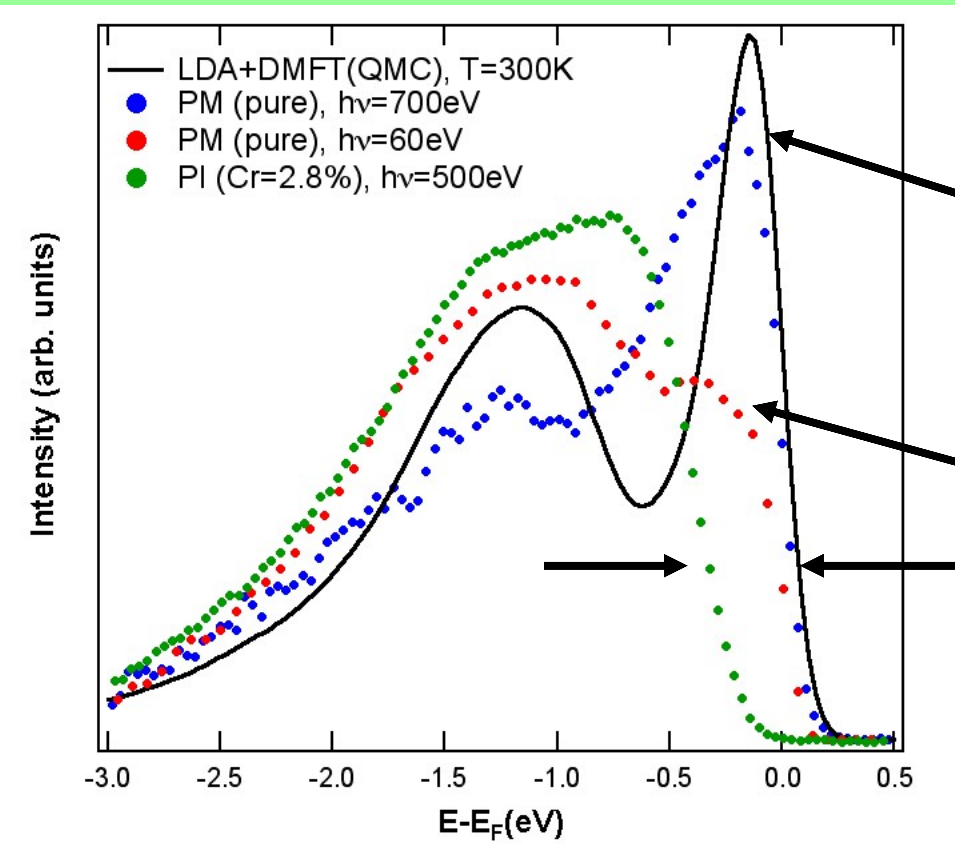
<u>but resolution not good at high photon energy at that time.</u>

Angle integrated bulk sensitive spectra for Mott transition in $(V_{1-x}Cr_x)_2O_3$

Experiment: SPring-8 BL 25SU (S. Suga)
- $h\nu$ = 500-700 eV total $\Delta E \approx$90 meV
  - Cleaved single crystals from P. Metcalf, Purdue

Mo et al, PRL (2003)
Vollhardt and Kotliar, Physics Today (2004)





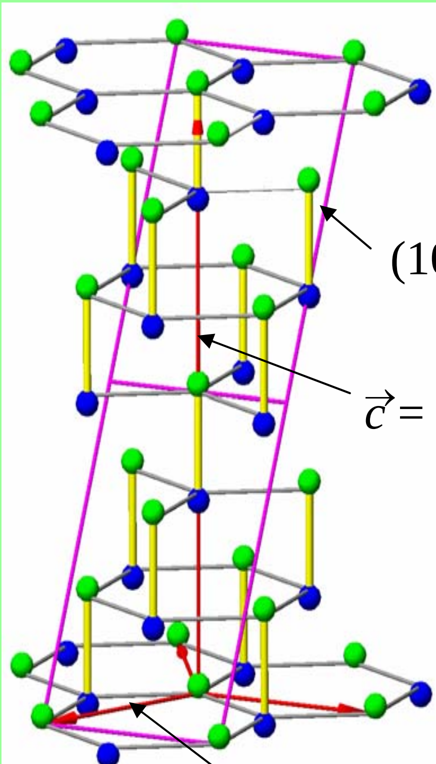
"Kondo peak" theory and experiment in M phase

Previous work, 30 years NO M phase peak

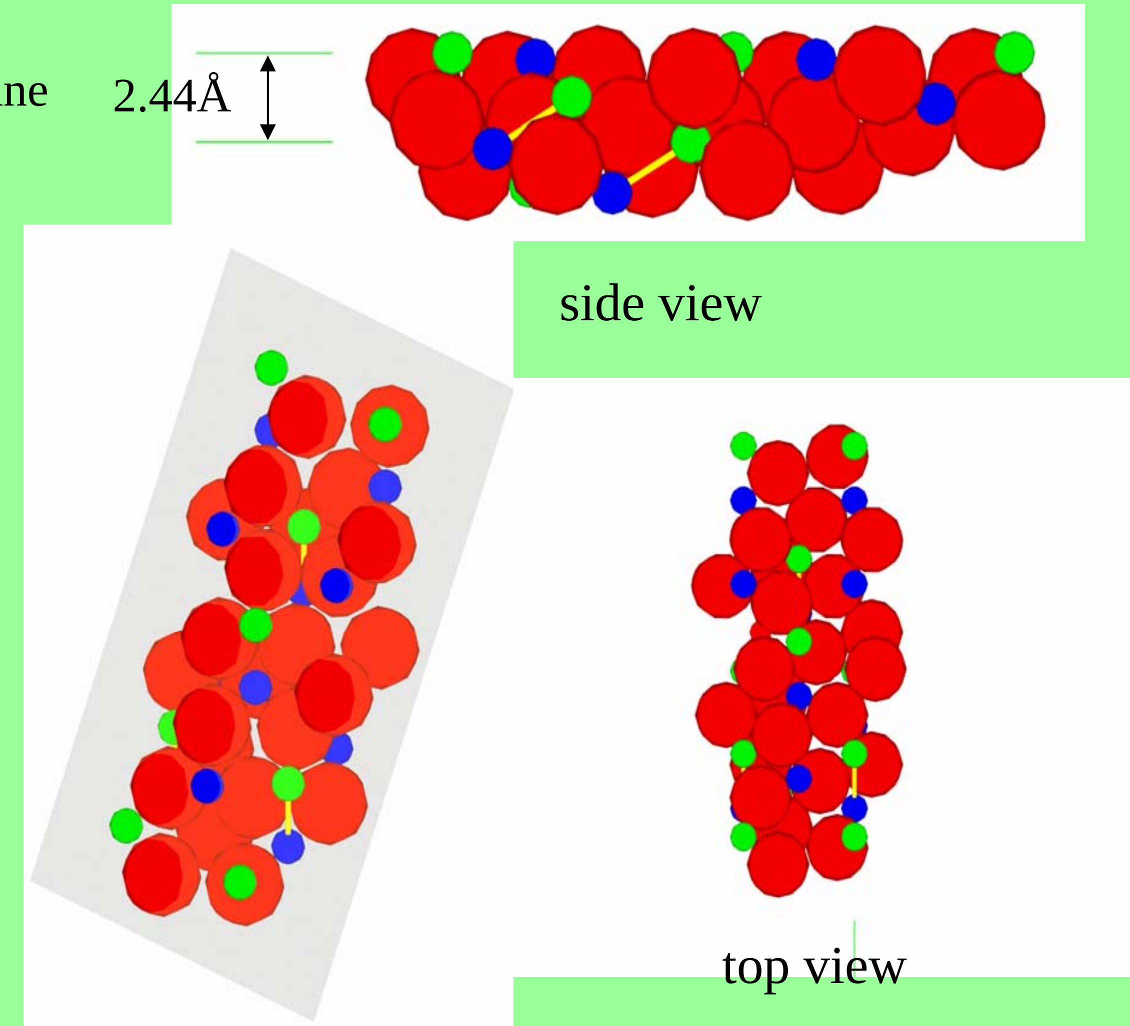
I phase GAP

Surface layer more correlated than bulk

Crystal structure and surface layer



surface-layer thickness =

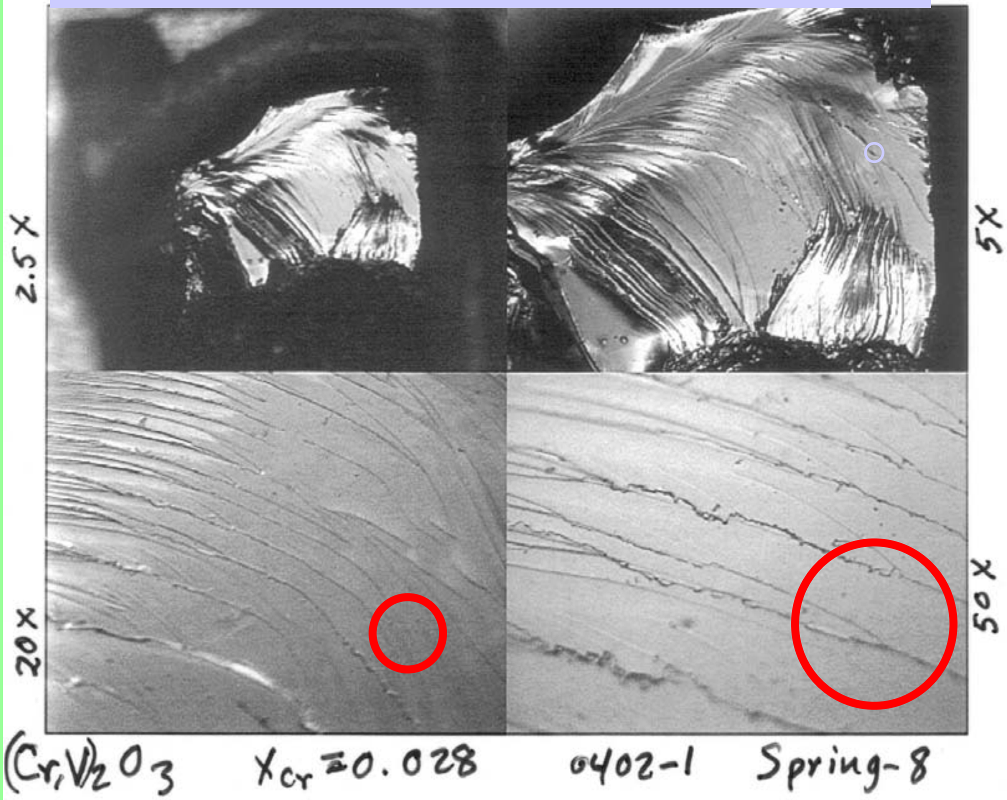


Vanadium

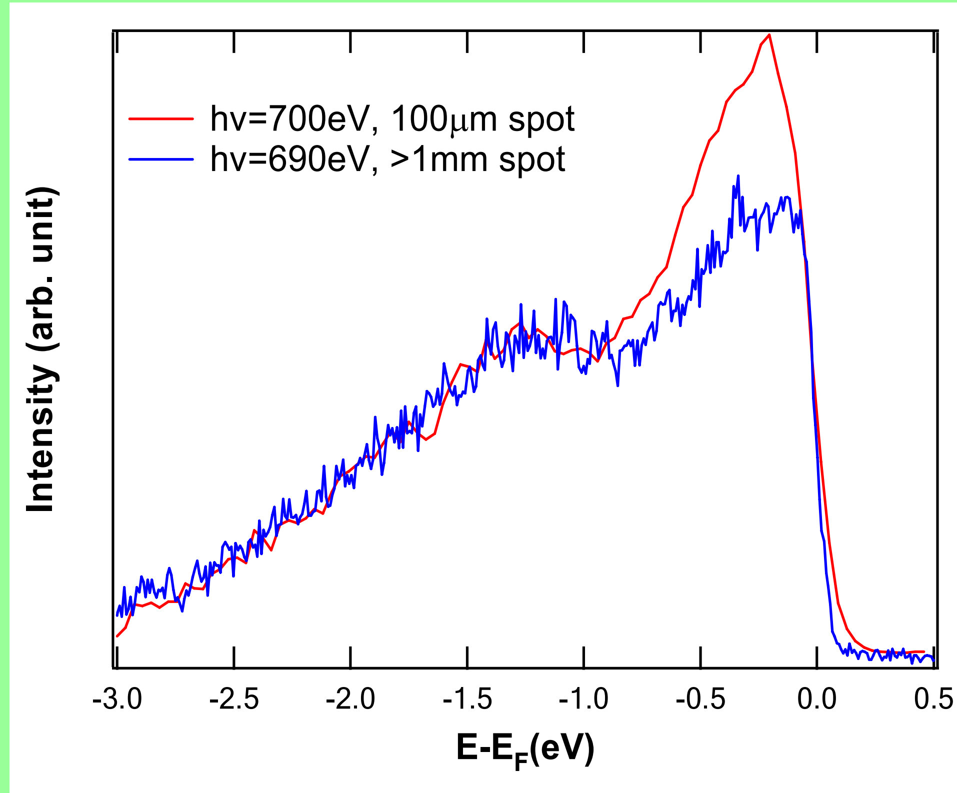
Oxygen

Small spot also essential for large E_F peak !

Optical micrograph—J.D. Denlinger



○ = 100 μm spot size



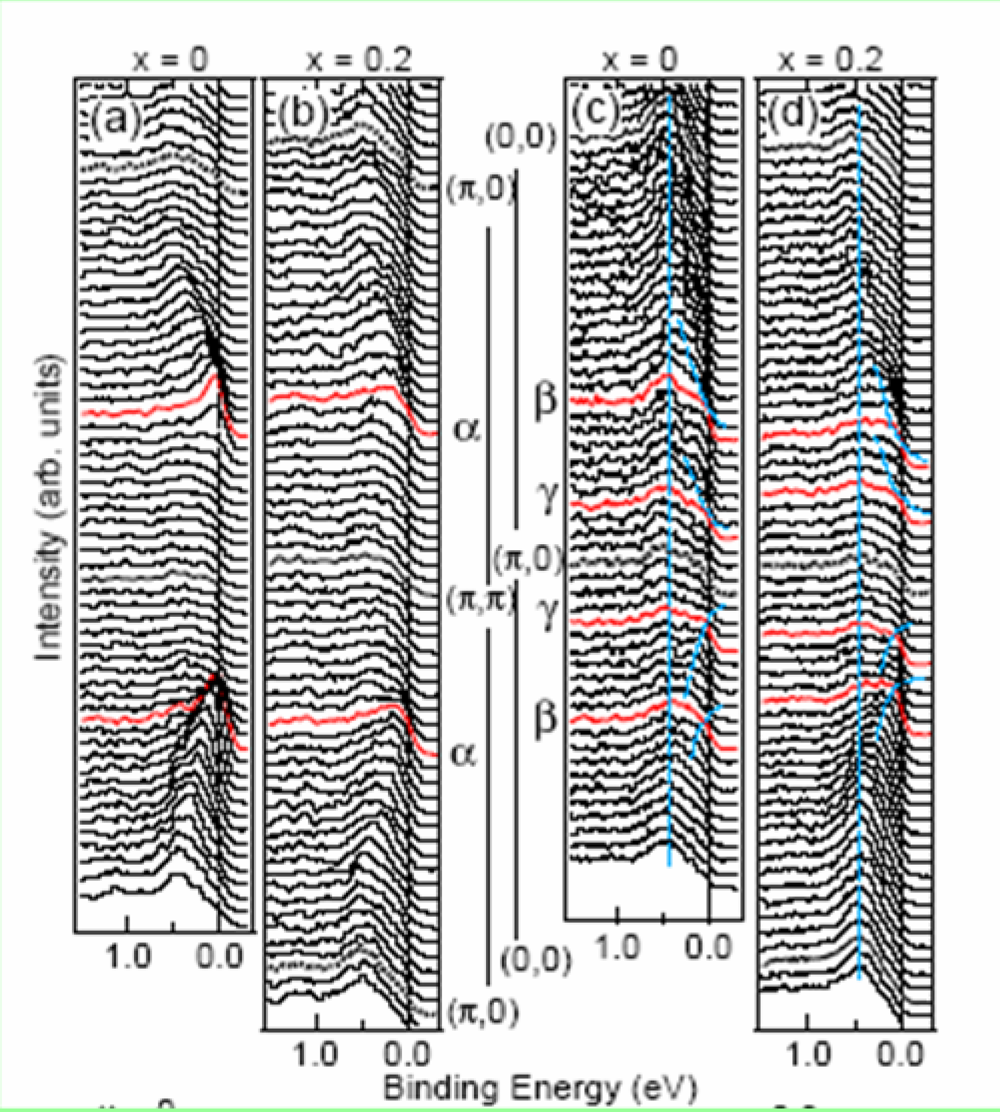
E_F peak much reduced with larger spot

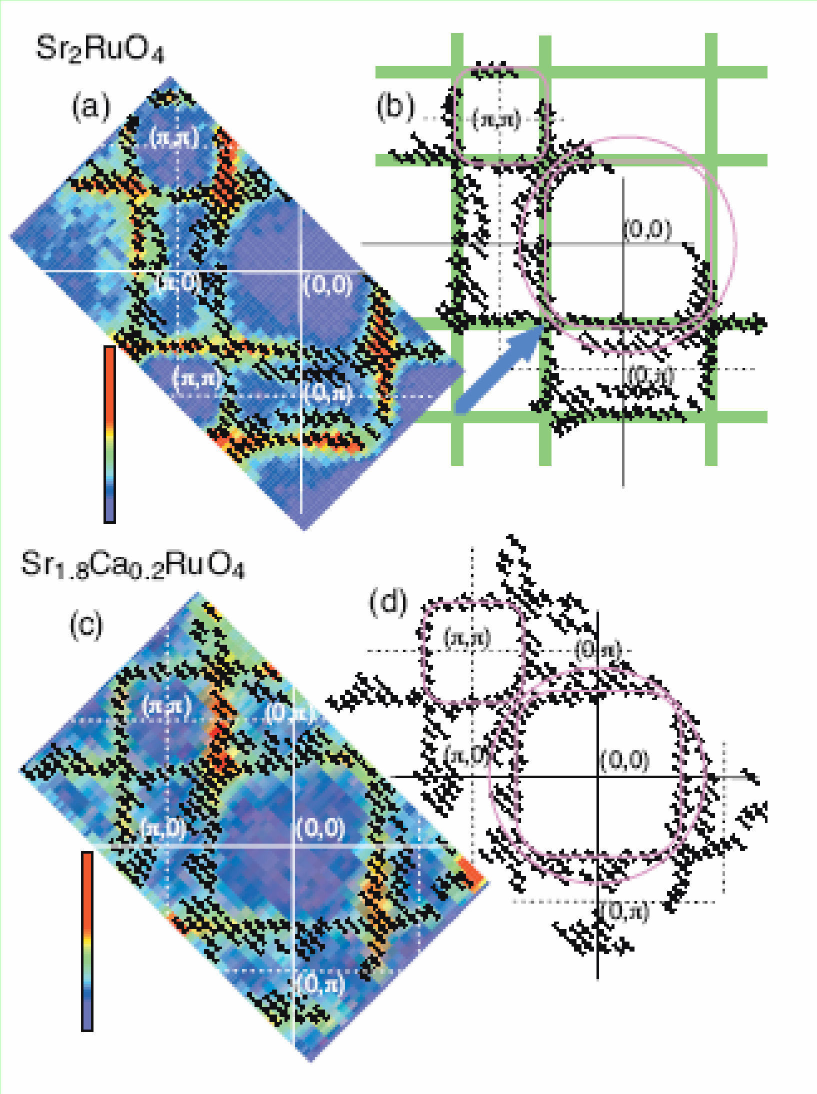
Difference for 300 eV to 500 eV range even larger

With small spot can select probing point to <u>avoid steps, edges, strain as much as possible</u>

Steps, edges have even lower coordination than smooth surface

High photon energy ARPES is possible!
E.g. $Sr_{2-x}Ca_xRuO_4$ (x=0, 0.2) Sekiyama et al, cond-mat/0402614



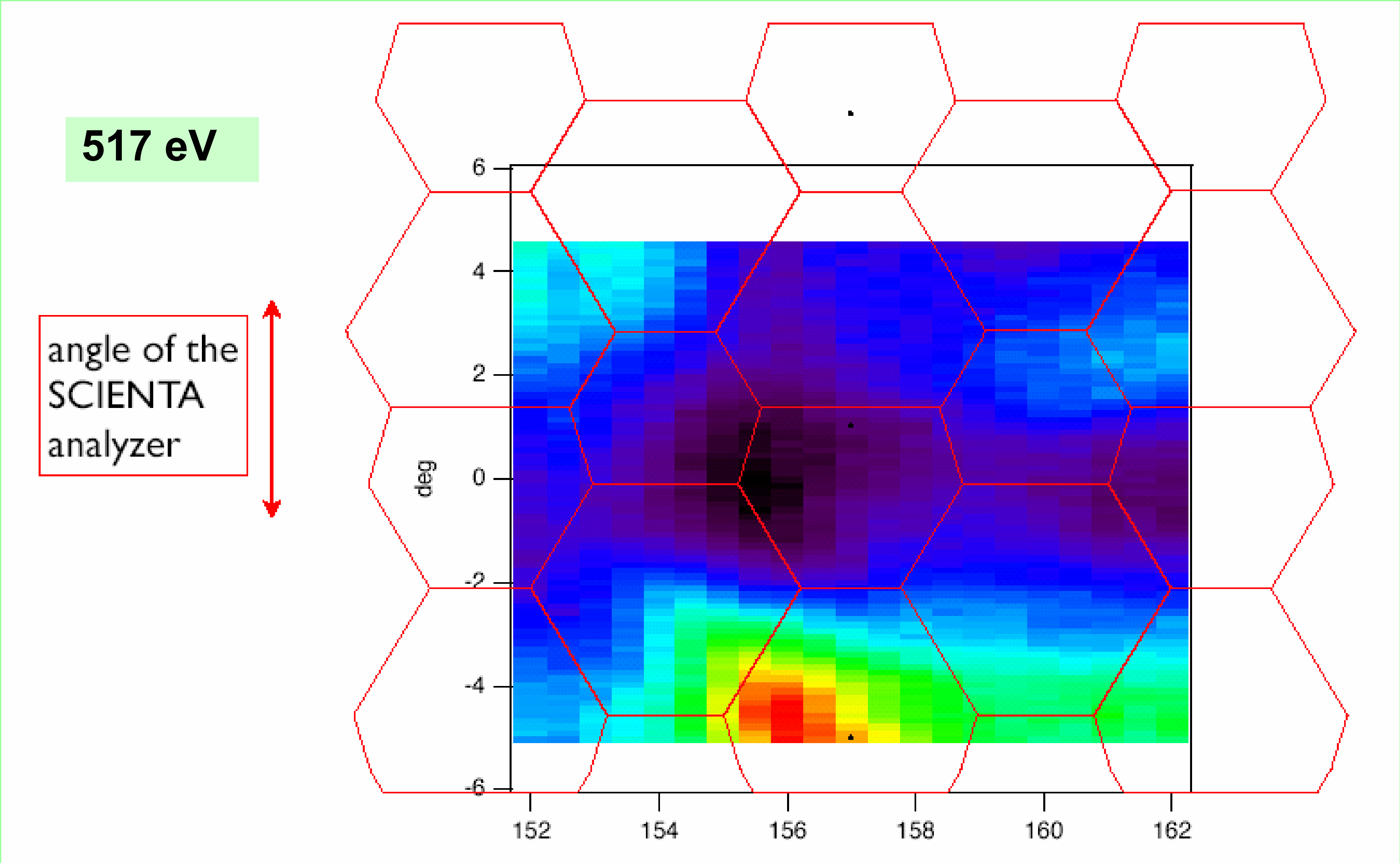


EDC's for various directions in Brillouin zone

Fermi surface maps: (b) and (d) are schematic comparisons to theory

Low photon energy -- quench surface states to see bulk electronic structure
High photon energy -- just cleave and measure

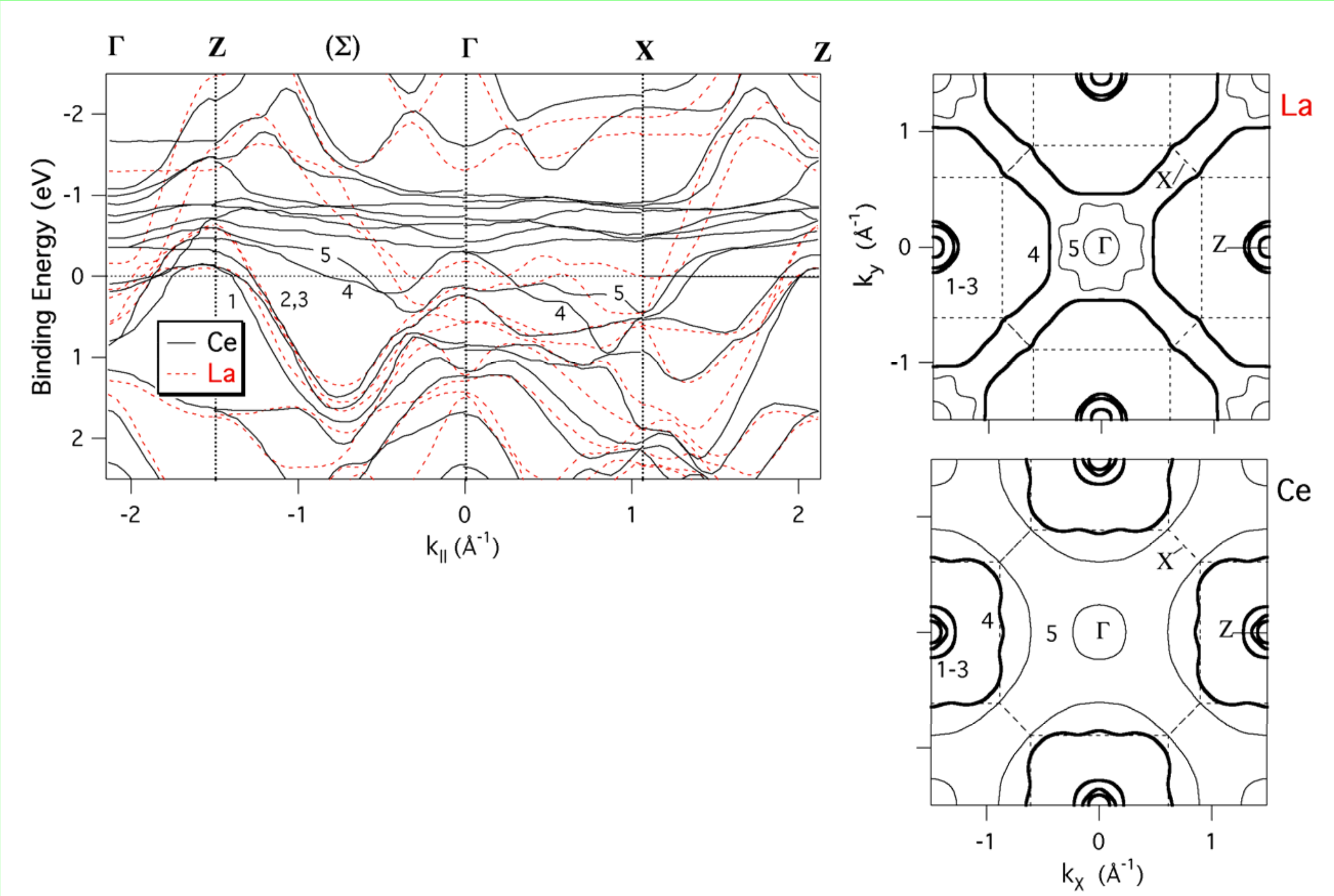
ARPES on V_2O_3



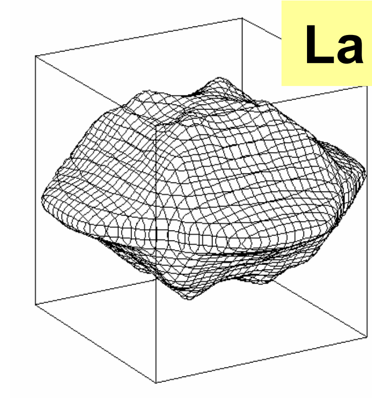
Have tried to FS map by ARPES at SPring-8

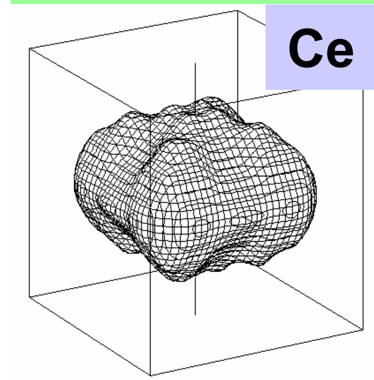
Hints of data but just not enough beamtime to do systematic job.

LDA for $LaRu_2Si_2$ and $CeRu_2Si_2$ compared



band 4
Z- hole pocket

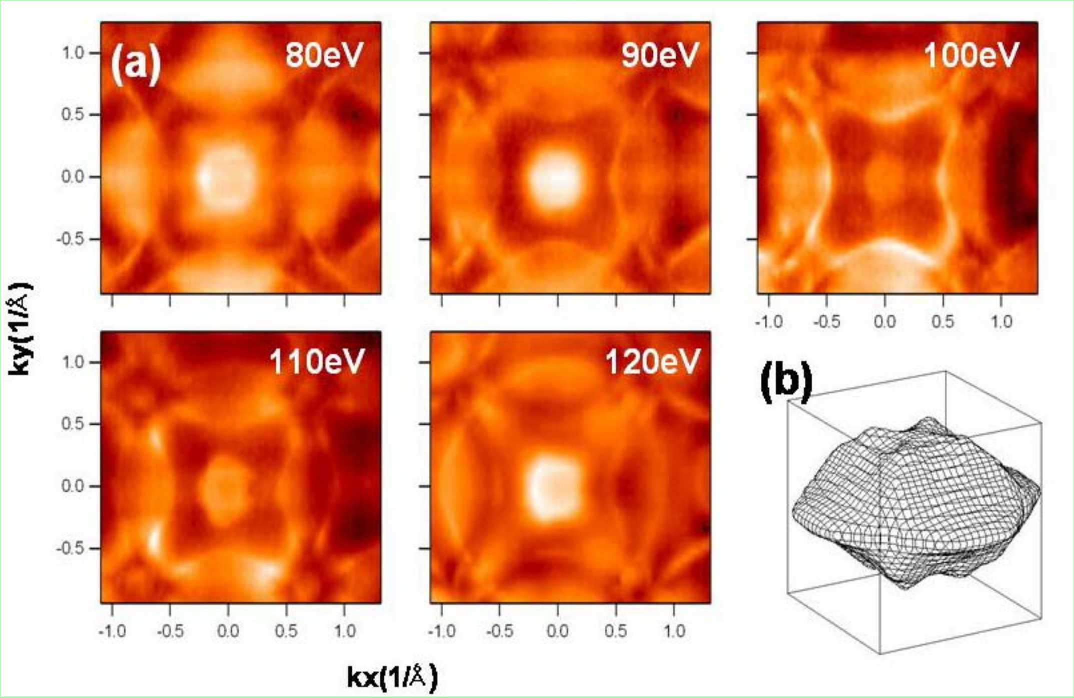




Overview from summary and review papers by Zwicknagl and her collaborators

$LaRu_2Si_2$

3D Fermi surface mapping



Full 3D character of FS observed by fine-angle maps at fixed photon energies & by fine photon-energy-step k_Z-dependent slice at fixed angle.

samples from J.L. Sarrao (LANL

Fermi volume change at Kondo temperature: the f-electron in $CeRu_2Si_2$

<u>Luttinger counting theorem</u> ⇒

f-electrons counted in Fermi volume
IF magnetic moments quenched

(as in Kondo effect)

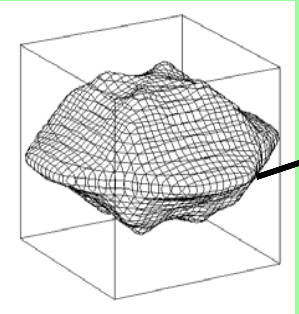
<u>Conjecture</u> (Fulde & Zwicknagl, 1988)

f-electrons <u>excluded from FS above Kondo temperature T_K</u>

Difficult to test with low-T dHvA.

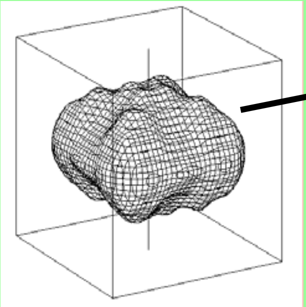
<u>paradigm</u> (dHvA) (Tautz et al,1995)

- <u>large</u> Z-point <u>hole</u> FS
  f^0 $LaRu_2Si_2$



LDA
"band 4" hole
Fermi surface
no f- electron

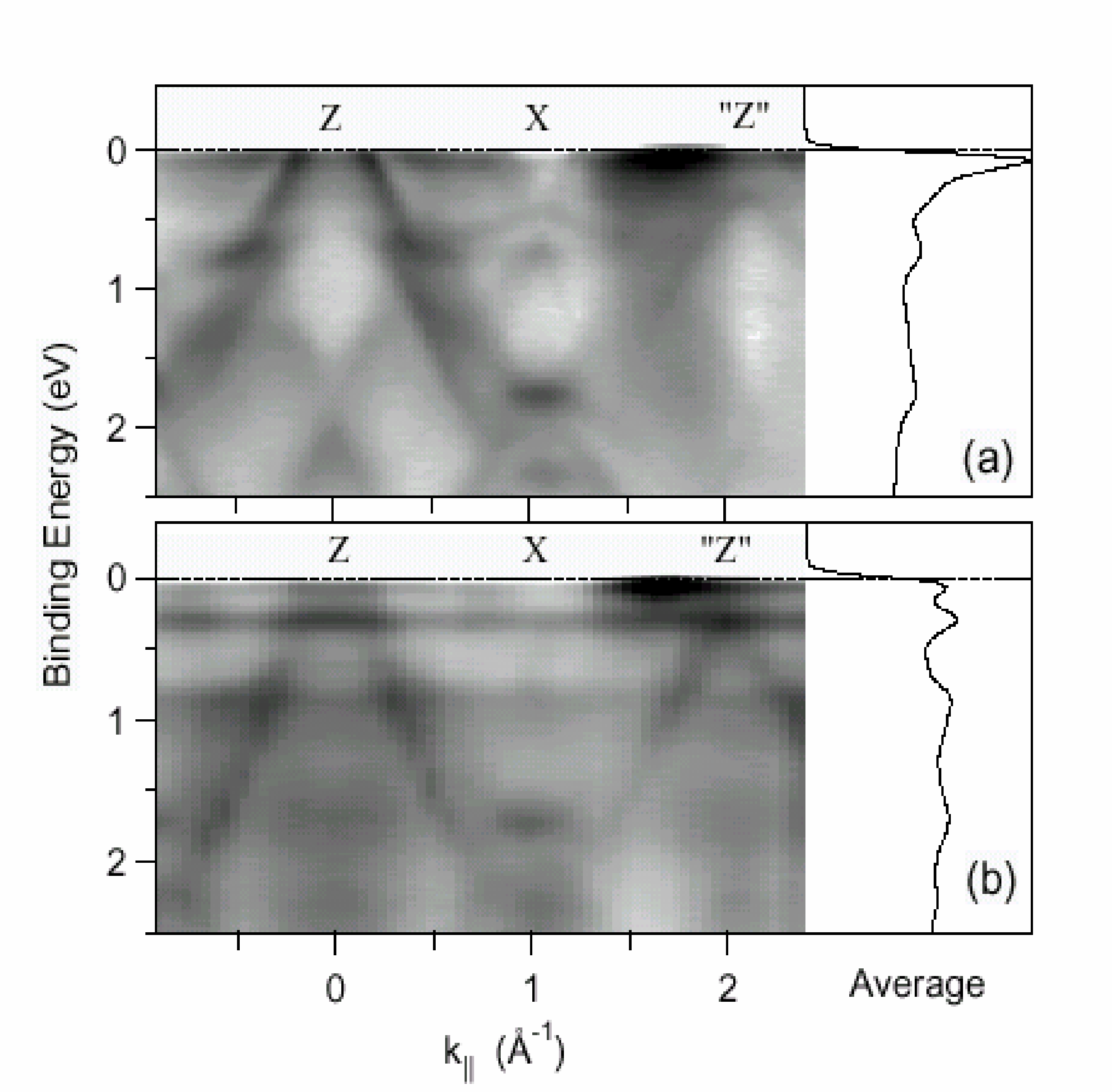
- <u>reduced</u> "pillow" <u>hole FS</u>
  counts ≈ ½ Ce f- electron
  in Kondo $CeRu_2Si_2$
  --at <u>temperature below T_K</u>



≈½ extra f-electron here

(≈½ f-electron in other multiply-connected complex FS piece)

$CeRu_2Si_2$ ARPES good and bad cleaves

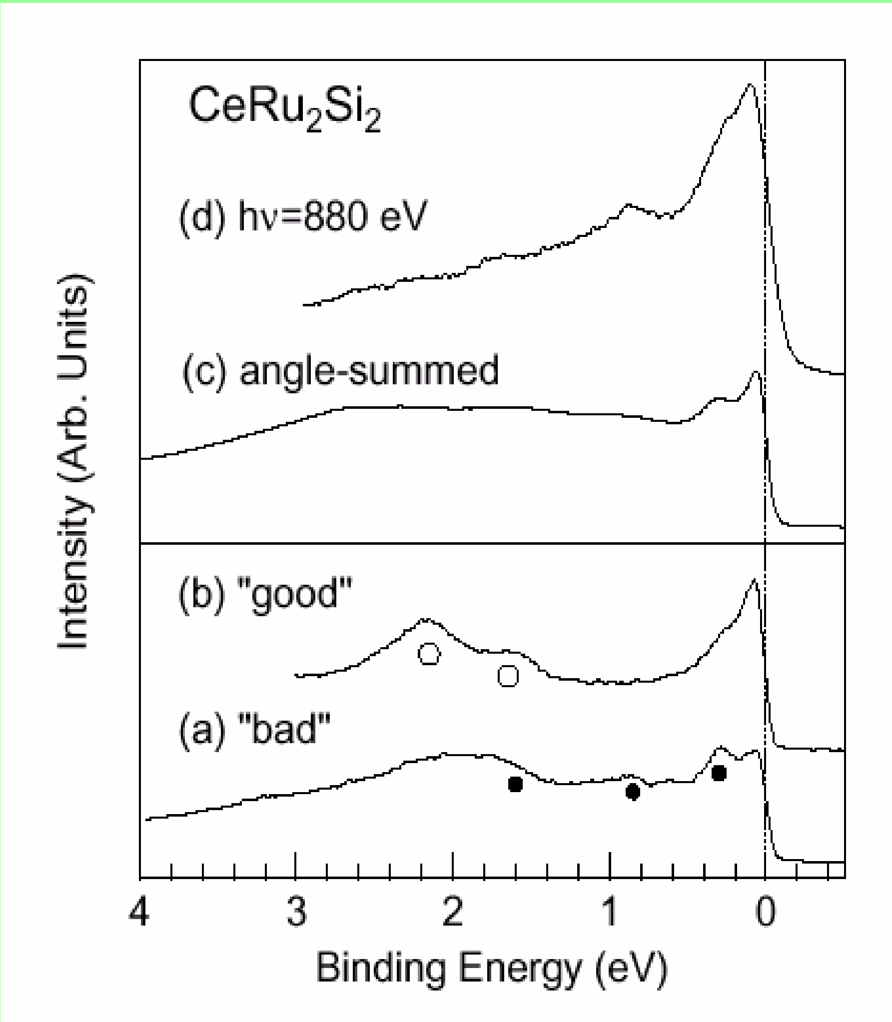


good

bad

Low hν OK for $CeRu_2Si_2$

Evidence that bulk behavior can be seen in 4d RESPES of <u>this</u> material



(d) Ce 3d edge RESPES with 0.2 eV resolution (consistent with SPring-8 data)

(c) angle summed 4d edge RES-ARPES

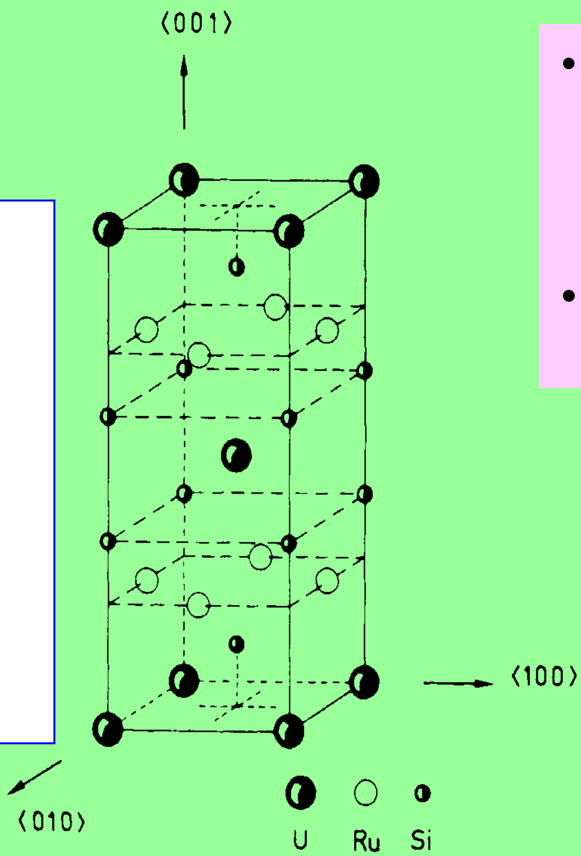
(a) and (b) ARPES from center of normal emission Z-point

J. D. Denlinger et al, Physica B 312-313, 670 (2002)

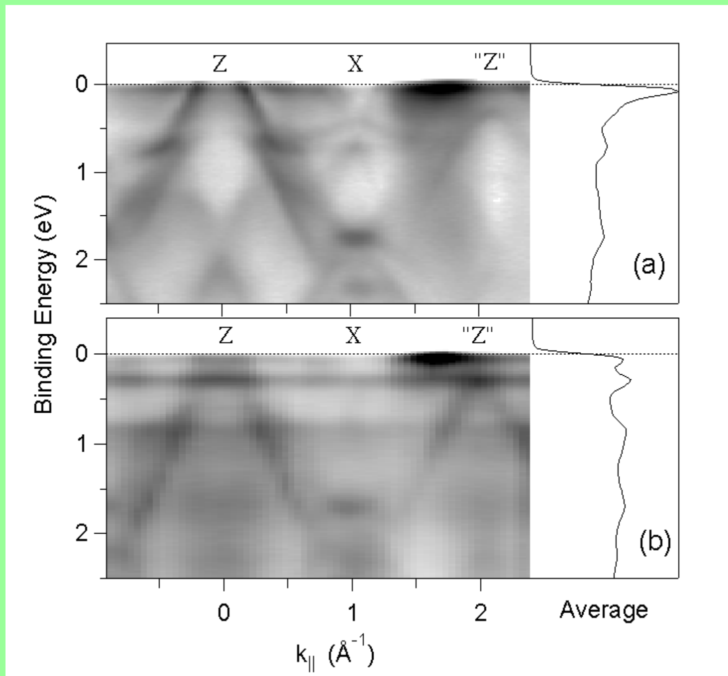
$CeRu_2Si_2$ why bulk at low $h\nu$?

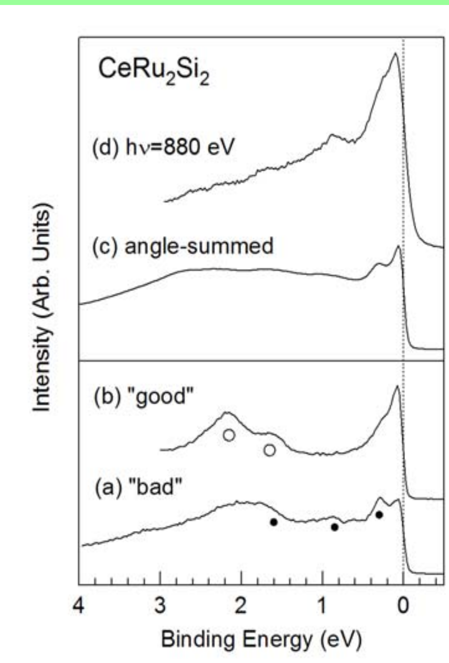
Two cleavage planes -- with and without Ce
i.e. buried active layer -- important for Bi 2212 cuprate

X
Si
Ru
Si
X
Si
Ru
Si
X

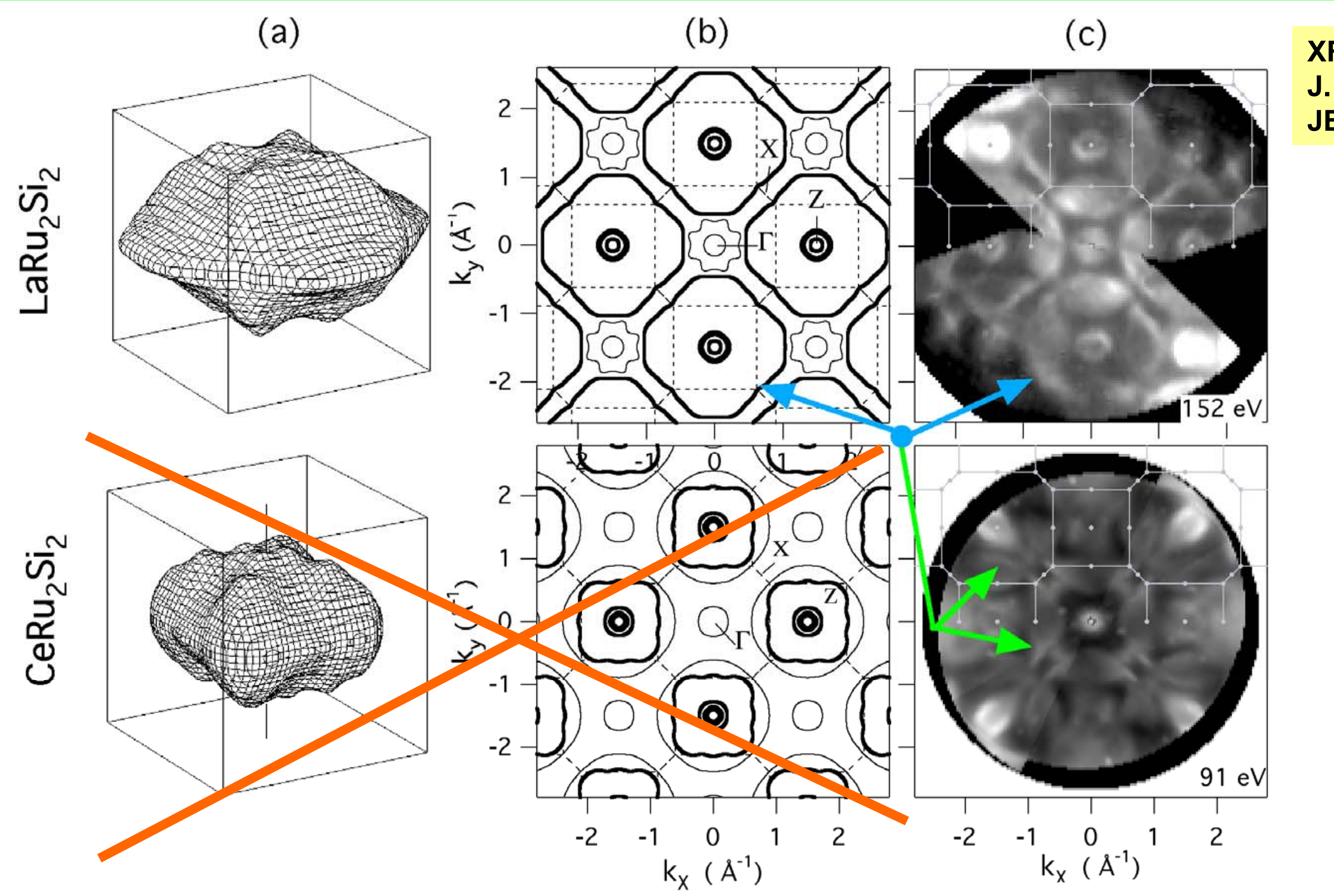


- **Atomic layer stacking in XRu_2Si_2 structure + preferential cleave between Ru-Si**
  $\Rightarrow$ no surface (less coordinated) rare-earth atoms (except for steps / surface roughness)
- **Bulk-like spectra obtained at even 100 eV similar lineshape to high photon energy spectra**





Same large hole FS for $LaRu_2Si_2$ and $CeRu_2Si_2$ for $T \approx 120K > 6T_K$ $\Rightarrow$ f-electrons excluded from FS!



XRu_2Si_2 review:
J. D. Denlinger *et al*,
JESRP 117, 8 (2001)

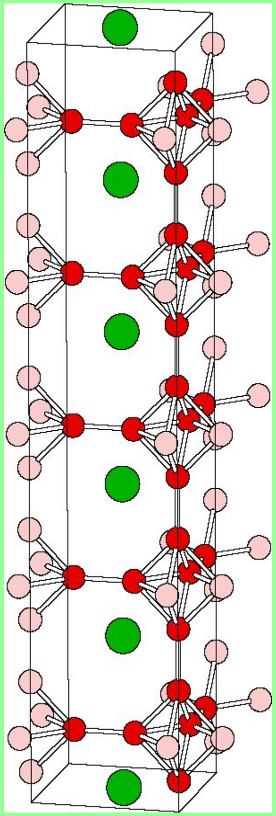
samples
J. Sarrao
LANL

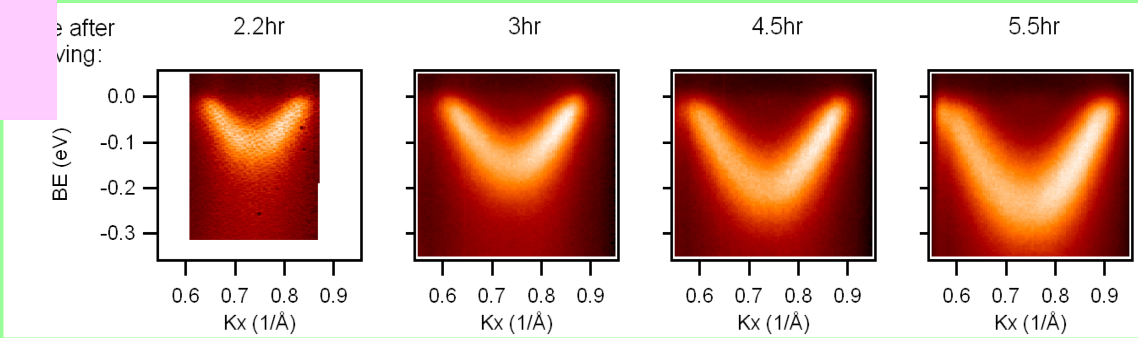
Same conclusion from 2d angular correlation of positron annihilation studies--
(Monge et al, PRB, 2002) but didn't actually measure the "pillow"

More surface effects: EuB_6

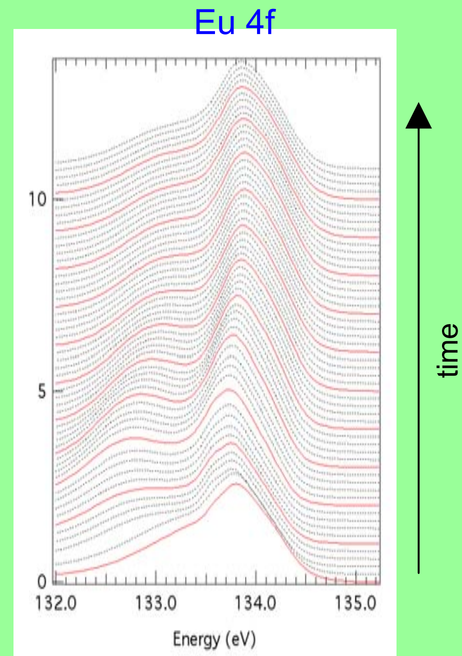
Time dependent relaxation of a polar surface

- Covalent bonded B_6
- Ionic bonding:
  Eu^{2+} & $B_6^{(2-)}$

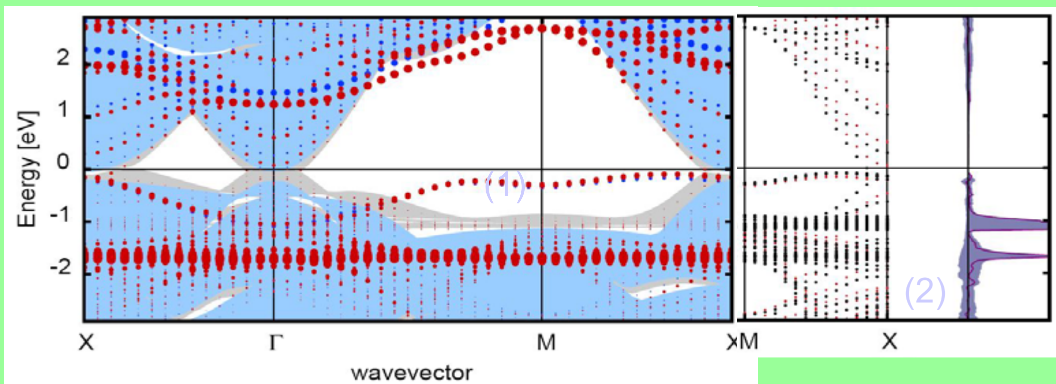




↑ Time-dependent size of X-point electron pocket

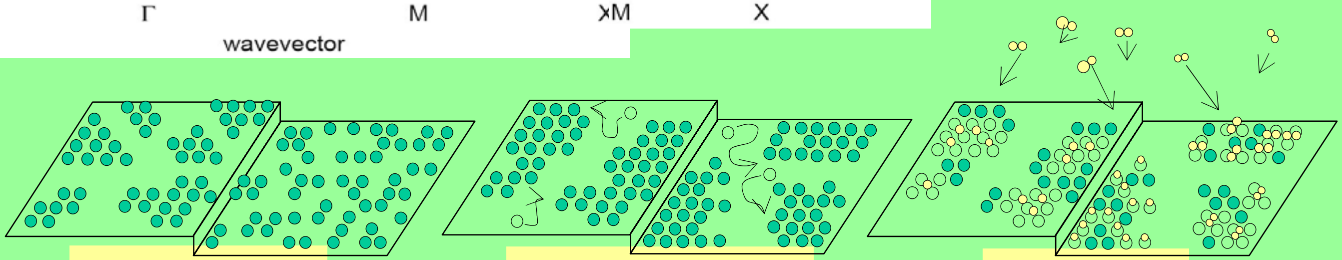


Time-dependent surface-shifted Eu 4f state →



← Surface slab calculation:
(1) surface state in bulk gap
(2) surface-shifted Eu 4f

Time-dependence Model →



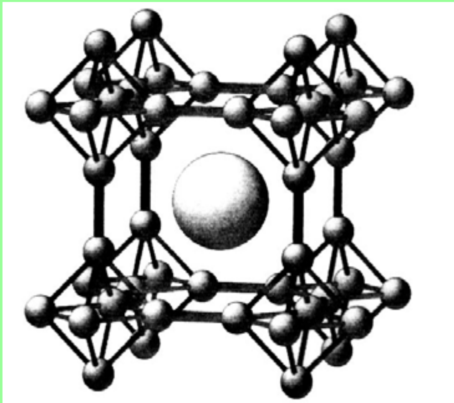
t = 0 (Cleave)
Statistically 50% Eu-terminated

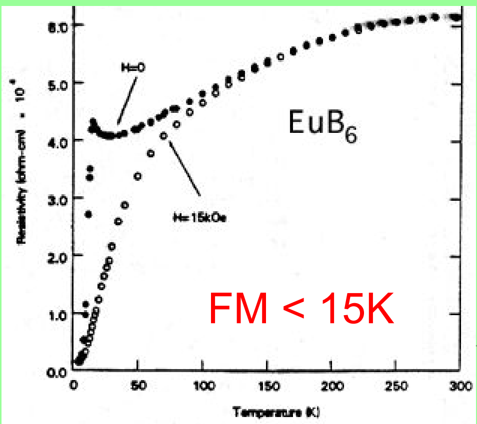
t < t*
Clustering of mobile surface Eu atoms

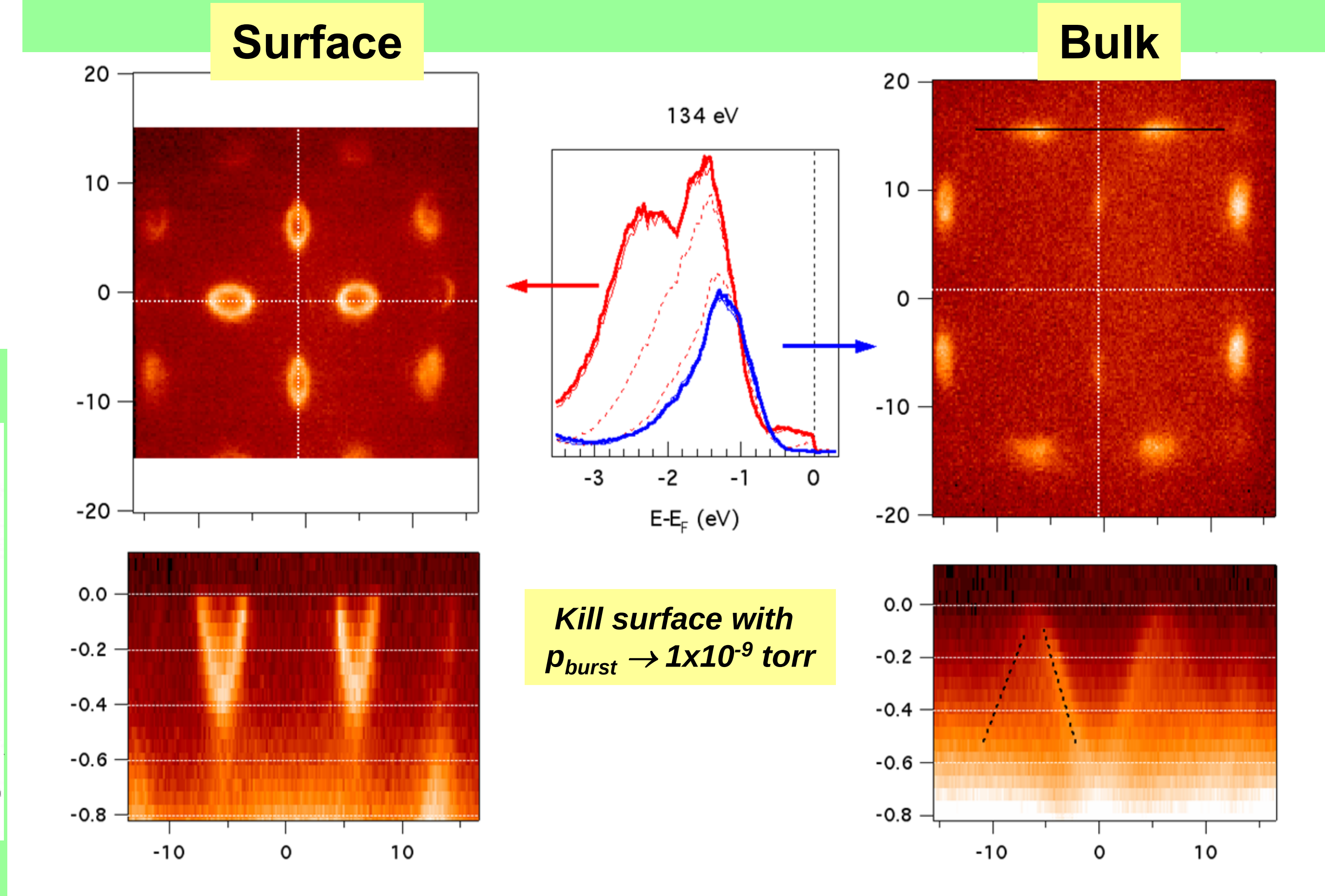
t > t*
Residual gas adsorption

w/ Z. Fisk (UC Irvine), B. Delley (Paul-Scherrer Institut), R. Monnier (ETH-Zurich)

EuB_6 --kill surface effects to see bulk



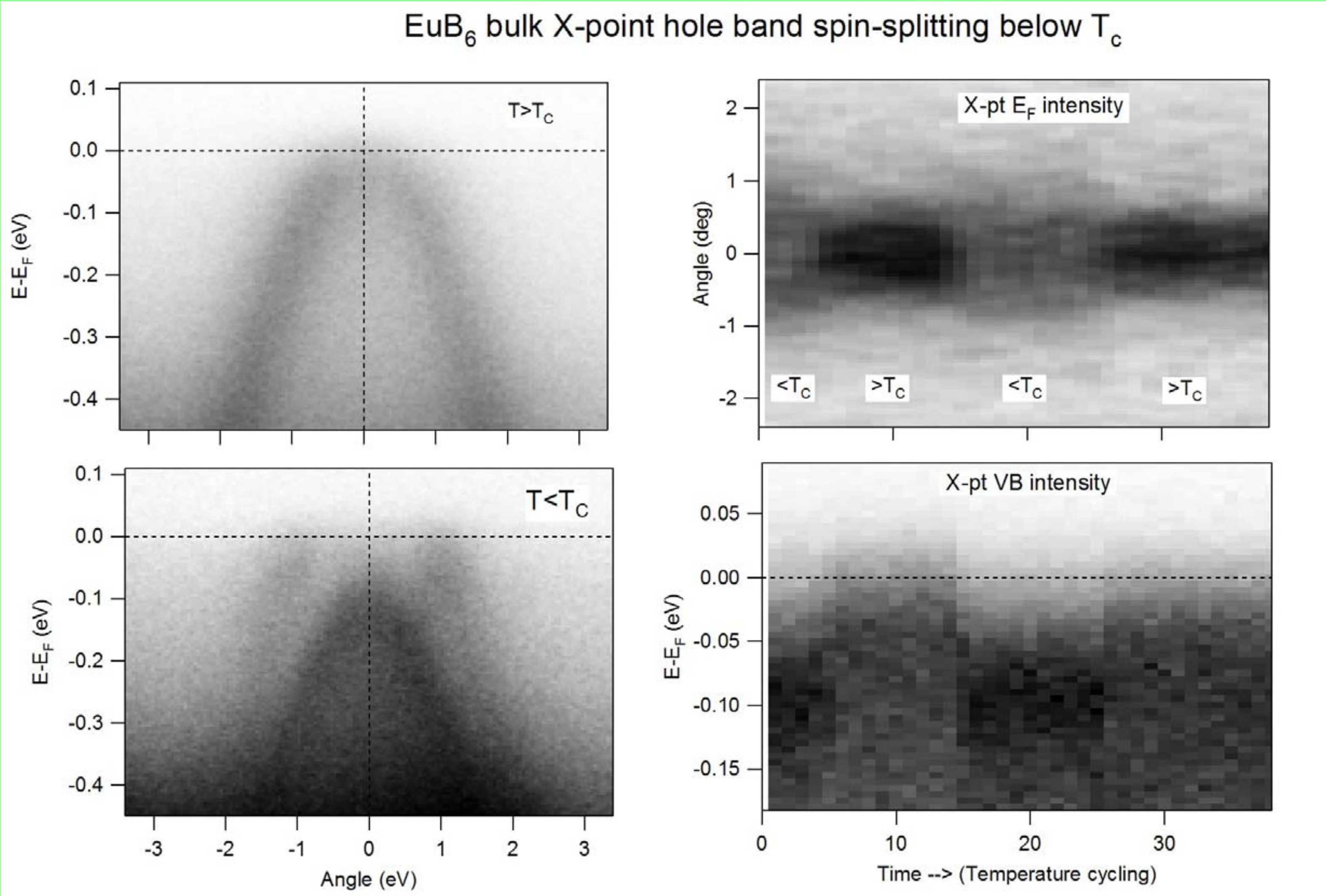




- **Surface: electron-rich Eu-termination ⇒ X-point electron pockets**
  + higher binding energy-shifted Eu 4f state
- **Bulk: hole-like pockets just touch E_F (p-type) ⇒**
  observe exchange splitting for $T<T_C$
  ⇒ bulk Ferromagnetism in EuB_6 likely from superexchange (like EuO)

w/ Z. Fisk (UC Davis), B. Delley (Paul-Scherrer Institut), R. Monnier (ETH-Zurich)

EuB_6 bulk valence band exchange splitting now observable below ferromagnetic T_c



YbBiPt

- 8 maps span full FS along <111> oriented cleave
  surface probed; bulk very near Yb 3+
- 3-fold symmetry & k_Z-stacking observed
  in Fermi surface
- First ARPES Fermi surface map of any Yb-compound
- Small photon spot essential to get this data

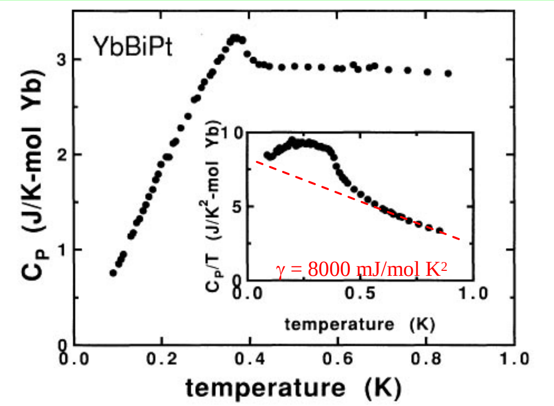
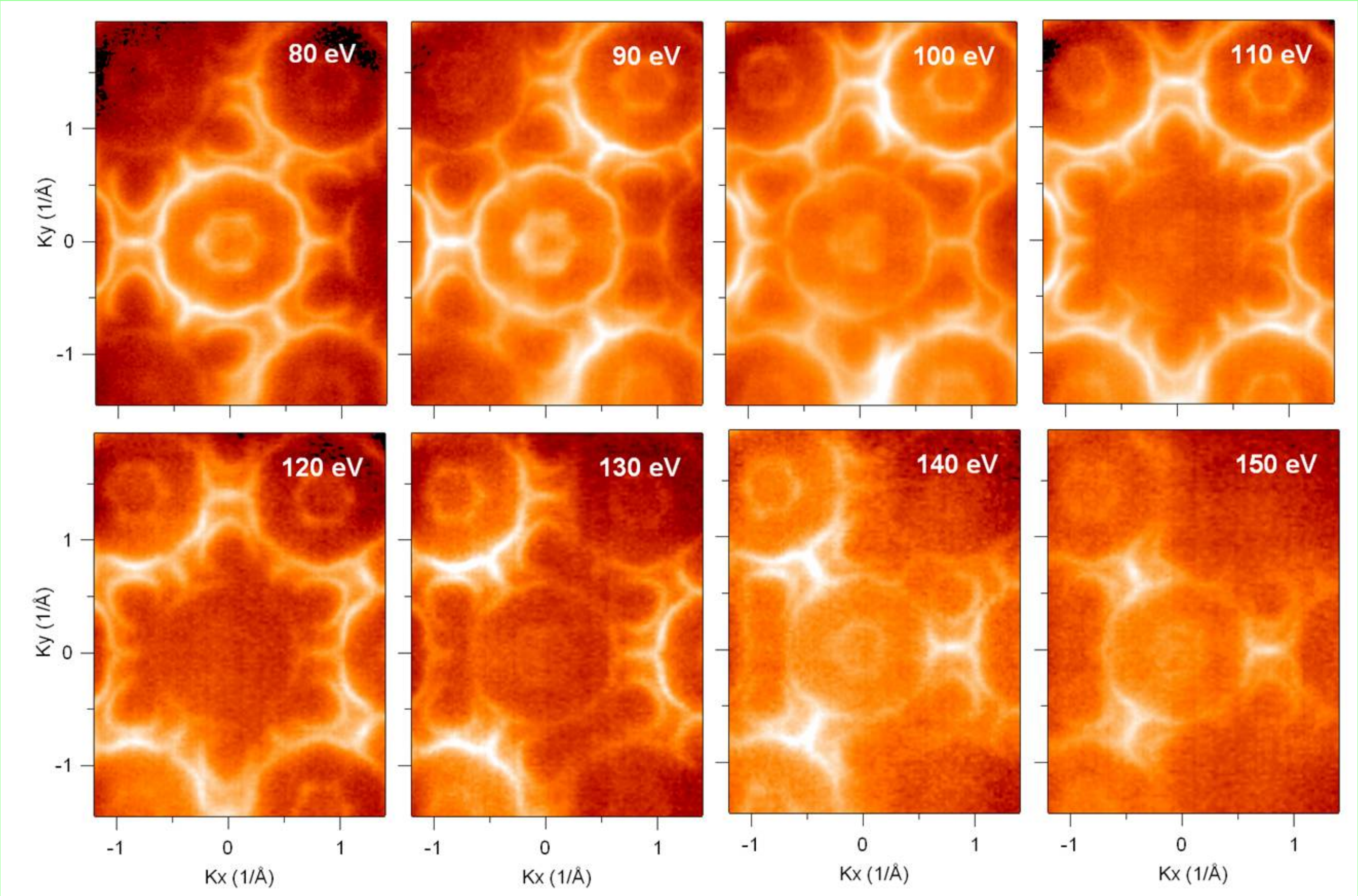
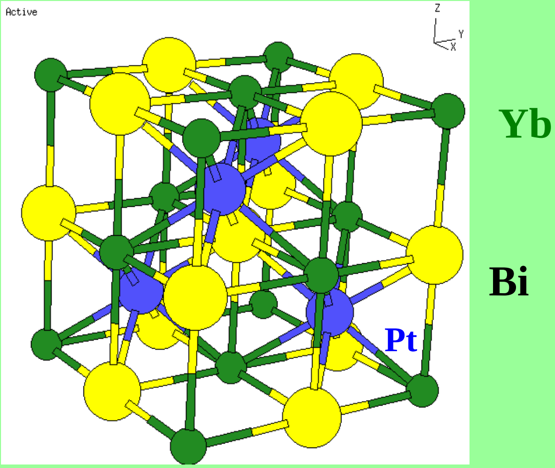


FIG. 2. Low-temperature specific heat $C_P(T)$ of YbBiPt between 0.09 and 0.85 K. Inset: Same data as C_P/T vs T.



heaviest Fermions
γ ~ 8000 mJ/mol-K



w/ Z. Fisk (UC Irvine)

Summary

Surface effects always lurking

- **"Ordinary" surface states are present (polar surfaces particularly unstable)**
- **Correlated systems especially vulnerable because of sensitivity to changes in bandwidth/U**
- **Steps and edges and other surface inhomogeneities can greatly enhance bulk to surface differences**
- **Buried active surfaces can give bulk data but usually require a "lucky cleave"**

High photon energies and very small photon spots offer best protection